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ENGINEERING AND DEVELOPMENT SUPPORT OF GENERAL
DECON TECHNOLOGY FOR THE DARCOM INSTALLATION
RESTORATION PROGRAM

Task 2. Desensitization of Explosive-Laden Soils/Sediments

Volume I

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Robert P. Relyea
Timothy G. Shea, Ph.D.

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10521 Rosehaven Street
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June 1983

Final Report
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Aberdeen Proving Ground, MD 21010

Prepared For:

Commander
U.S. Army Toxic and Hazardous Materials Agency
Aberdeen Proving Ground (Edgewood Area), Maryland 21010

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Explosives	Sediment	Gama Irradiation
TNT	Treatment Technologies	Wet-Air Oxidation
RDX	Alkaline Digestion	Complexing-Hydrolysis
Nitrocellulose	Chemical Reduction	Biological Treatment
Desensitize	Chemical Degradation	Fenton's Reagent

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This report presents a technical and economic evaluation of desensitization processes for explosive contaminated lagoon sediments. Chemical reduction, alkaline digestion, complexing-hydrolysis, aerobic biological, anaerobic biological, gamma irradiation, and wet-air oxidation were evaluated by comparison to incineration. Ultra-violet irradiation, oxidation, thermal degradation, surfactant-oil complexing, detonation, composting and open burning were evaluated to a lesser extent.

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SUMMARY

The objectives of Task 2 were the development, evaluation and ranking of processes for the desensitization of explosive-laden lagoon sediments. Processes were developed by matching desensitization concepts with representative lagoon scenarios and schemes for contacting the sediments with desensitizing agents. Chemical, biological and thermal processes were evaluated by comparison with each other and with incineration, the baseline process. The evaluations were based upon the attainment of performance measures which included: flexibility, degree of desensitization, implementation time, complexity, risk acceptability, state-of-the-art, cost and disposability. Processes were then rank-ordered and recommended for experimental development upon the basis of the evaluation.

Seven basic concepts and their representative processes were evaluated and ranked during the study: (1) chemical reduction; (2) complexing-hydrolysis; (3) alkaline digestion; (4) gamma irradiation; (5) aerobic biological treatment; (6) anaerobic biological treatment; and (7) wet-air oxidation. In addition ultraviolet irradiation, oxidation, detonation, open burning, thermal decomposition, composting and surfactant-oil complexing were evaluated to a lesser extent.

Gamma irradiation, chemical reduction, complexing-hydrolysis and alkaline digestion were consistently ranked higher than incineration, the baseline process. The biological alternatives could not be reasonably evaluated due to the limited amount of kinetic data available. Accordingly, it is recommended that bench-scale studies be performed to further the engineering development of processes for chemical reduction, gamma irradiation and anaerobic and aerobic biological waste treatment.

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CHAPTER 1

INTRODUCTION

Soils and sediments contaminated with explosives are present in old wastewater lagoons at many government installations. These are a legacy from past operations involving the manufacture, load, assembly and pack processing of these compounds and the demilitarization of ammunition. The reactivity of the contaminated soils and sediments mandates that desensitization technology be developed for safety, environmental and economic reasons.

Desensitization is a form of primary treatment essential to the implementation of any program for the remediation of groundwater contamination and ultimate closure of these lagoons. The steps necessary to accomplish desensitization include the retrieval of the sediments or otherwise gaining access to the explosives and the chemical, biological or thermal processing by which desensitization takes place. The terms "initial materials handling" and "secondary materials handling" are used in this report to define the first handling of the raw material and the subsequent handling steps prior to completion of desensitization. The end result of desensitization is the generation of liquid effluents, side-streams and/or residual solids; any of these may be toxic in nature as well as unacceptable for discharge or disposal without further treatment because of organic, solids or nitrogen content, pH, or some other characteristic.

The present report addresses desensitization as its central theme. Chemical, biological and thermal processes for desensitization are compared with incineration; the latter as a baseline system. The treatment of liquid effluents, sidestreams and residual solids from a desensitization process is called "post-desensitization treatment" in this report. Post-desensitization treatment is addressed herein only as coincidental to the desensitization effort. As a further matter of definition, desensitization and Post-Desensitization Treatment are only two of the elements of an Installation Restoration system; the others include measures

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such as containment, secure landfill disposal of residual solids and
permanent closure of the site.

OBJECTIVES

The general objectives of this task are to:
o Develop concepts for the desensitization of lagoon soils and
sediments that can render them amenable for safe disposal, or for
further treatment without hazard of explosion.
o Evaluate the concepts by comparison and then rank-order them.
o Recommend concepts to be studied experimentally for purposes of
determining which have immediate application and which should be
brought forward to the field demonstration stage.

The specific objectives are as follows:
o Conduct a literature search to identify existing treatment
technology and concepts for desensitizing the explosives TNT, RDX,
HMX and nitrocellulose.
o Review existing installation survey data and conduct interviews
with USATHAMA personnel to develop background information.
o Develop a basis for classification and categorization of the
desensitization problems.
o Provide recommendations for treatment criteria.
o Characterize all identified desensitization concepts.
o Identify those concepts that should be considered for laboratory
evaluation.

ORGANIZATION

This report is organized into three volumes, of which this is Volume
One. This volume is the Technical Report and contains an analysis of each
identified technology and the development and evaluation of alternatives
for desensitization. Volume Two contains the Appendices, which are
comprised of the design and cost analyses, while Volume Three is the
bibliography.

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CHAPTER 2

APPROACH

PROBLEM SETTING

The task of desensitizing soils and sediments from lagoons is compounded by the relative uniqueness of each of the three to four hundred lagoons in existence in the United States. The number, size and characteristics of the lagoons vary from site to site. Depending upon the history and variety of processing operations at a specific site, lagoons were either dedicated for the treatment of one waste stream or of the wastes from several processes. The concentrations and types of explosives present vary from one location to the next; in some cases only nitrocellulose or TNT are present, but in other cases TNT, RDX, HMX and other explosives or propellants are contained in the sediment. Wastes and byproducts from explosives processing or other operations such as isomers of TNT to heavy metals (mercury, cadmium, lead, etc.) and phthalates (used to gelatinize nitrocellulose) can also be present. The wastewater discharges to the lagoons may have been continuous or intermittent and from either one or a combination of several processes. The operational history of a lagoon will affect the concentration gradient of explosives in the sediments.

The physical factors characterizing a lagoon, such as underlying soils, type of liner, water table elevation and side and bottom permeability, also vary widely. In most cases, these characteristics are unique for each and every lagoon. The depth to the water table below the lagoon is also an important and variable characteristic. The potential presence of unexploded ordnance (UXO) and pieces of tramp metal requires that a careful survey of each lagoon be performed to confirm the situation. Once identified, UXO's must be removed by Army Explosive Ordnance Disposal (EOD) Personal. Compounding these circumstances are the lack of precedents and safety procedures for the handling and treatment of explosives-contaminated sediments and the absence of a workable definition of what "desensitization" means. This situation mandated that a broad and relatively unconstrained examination be made of technologies that would plausibly apply to the desensitization problem.

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CHARACTERISTICS OF EXPLOSIVES

A summary of the characteristics of the common explosives is presented in Table 1 and their chemical structures are illustrated in Figure 1; TNT, RDX, HMX and NC (nitrocellulose) are of specific interest herein. The common characteristics of these four explosives are that they are significantly more dense than water and vary from slightly soluble to insoluble in water. These properties become uniquely important to the development of desensitization concepts as evidenced in Chapter 3.

CONCEPT DEVELOPMENT

A generalized model for the selection of alternative concepts for desensitization is presented in Figure 2. The concept development is initiated by matching the characteristics of the lagoon with the basic desensitization concepts available and identifying the feasible thermal, chemical, and/or biological processes to be considered. The next step is the identification of all feasible contacting methods for each identified process. Once the contacting process combinations are identified, preferred initial materials handling methods are selected for contacting of the explosive in the desensitizing process. At this point, any desired method for process enhancement (e.g., heat) is introduced. The water control measures necessary for implementation of the selected initial materials handling methods are then identified; construction of dikes, drainage of the lagoon, etc. Each initial materials handling method can support a number of basic desensitization and post-desensitization treatment systems. Consequently, it is necessary to assess these in relation to the attainment of selected performance measures so that the feasible alternatives can be defined and rank-ordered.

The critical elements of the concept development process are the classification of the sites, the types of desensitization processes available, the feasible contacting methods and suitable performance measures. Each is described briefly below and developed further in subsequent chapters.

TABLE 1. CHARACTERISTICS OF EXPLOSIVES

Common Name	Chemical Name	Molecular Weight	Cast Density (g/ml)	Solubility in Water @ 20°C (g/100g water)
TNT	Trinitrotoluene	227	1.560	0.013
RDX	Cyclonite	222	1.816 [1]	0.0076 @ 25°C
HMX	Homocyclonite	296	1.870	Insoluble
NG	Nitroglycerin	227	1.596	0.173
NC	Nitrocellulose	297 [2]	1.600 [3]	Insoluble
NGu	Nitroguanidine	104	1.715 [1]	0.40 @25°C
Tetryl	Tetranitro Methylaniline	287	1.62	0.0075

Notes:

1. Crystal density

2. Per fully nitrated anhydroglucose unit

3. Dependent upon the liquid used for measurement and the degree of nitration

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FIGURE 1. STRUCTURES OF EXPLOSIVES (ARMY TECHNICAL MANUAL, 1967)

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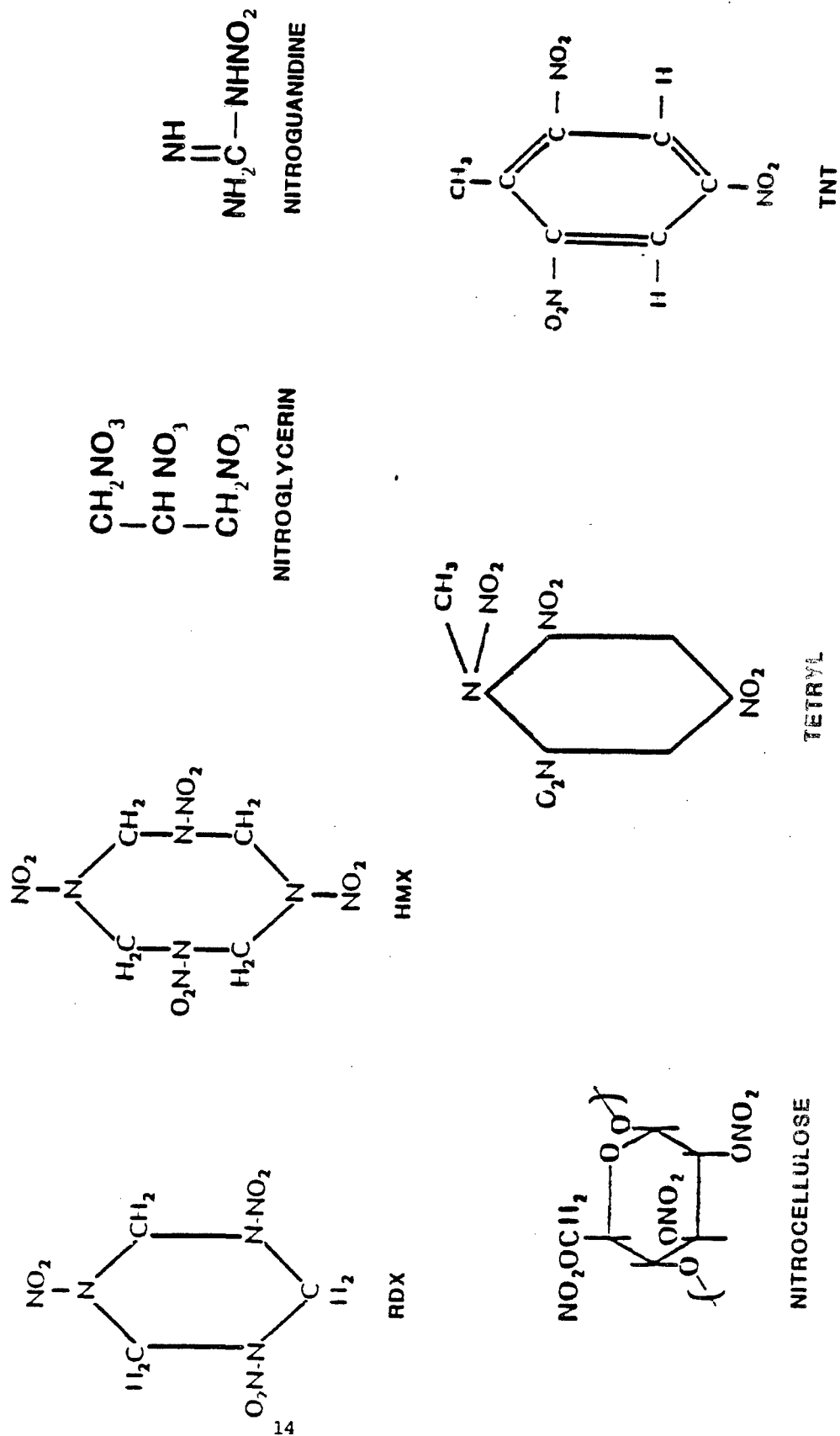
FIGURE 2. GENERALIZED MODEL FOR SELECTION OF ALTERNATIVES

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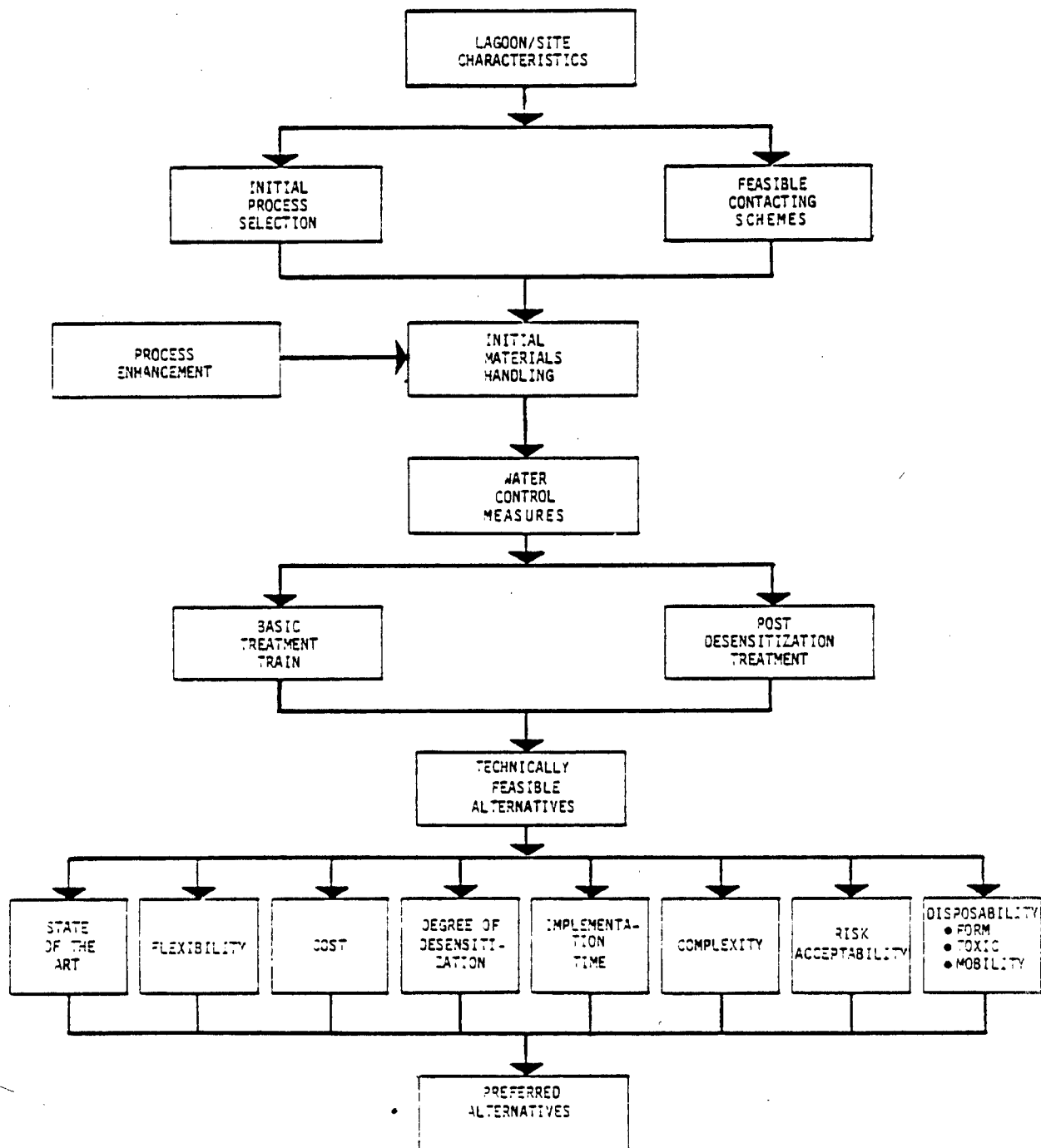
CLASSIFICATION OF SITES

The initial materials handling activity prior to desensitization is determined primarily by the characteristics of the lagoon. Due to the diversity of lagoon characteristics, a number of materials handling activities must be considered, and few if any will be feasible for all lagoons. It is first necessary to identify those characteristics which determine the feasibility of an initial materials handling activity, i.e., how the materials will be handled for the first time.

The proposed concept is the classification of each site to the greatest extent possible in terms of the following characteristics:

- Number of lagoons at site
- Size and volume of lagoons
- Presence of standing water
- Lagoon liner, if any
- Soil type and depth
- Depth to water table
- Explosives and propellants present
- Concentration of explosives and propellants
- Moisture content of sediment
- Depth of contamination
- Presence of toxic metals (and other toxic substances)
- Availability of a process wastewater treatment plant and other support services
- Presence of unexploded ordnance (UXO) and tramp metal
- Permeability of the banks and the bottom of the lagoon

The characterization of all sites is not feasible at this time due to the high costs involved. However, a certain amount of information is available from previous characterizations. This information is summarized in "Lagoon Characteritization Data," (FSE, 1982). The principal observations to be made from the summary are as follows:

- The majority of the sites contain more than one lagoon

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o   Clay is the predominate soil type

o   About half the lagoons are dry and half contain standing water

o   The majority of the lagoons for which data are available contain TNT

o   The explosive content of the sediment is less than one percent in the majority of the lagoons for which data are available

o   A wastewater treatment plant is located on a majority of the sites

CONVERSION PROCESSES

Each desensitization concept or alternative is based upon a conversion process. Conversion processes are defined as those chemical, biological, or thermal transformations in which desensitization occurs. A feasible conversion process must be selected prior to the development of an alternative. Not all conversion processes are universally applicable; therefore, the initial selection must be based upon the type(s) of explosives present in the sediment and other information to be obtained from the lagoon characterization data. Treatability assays would possibly be conducted to test the feasibility of a preferred conversion process and develop the criteria needed to specify it. Examples of these criteria are chemical requirements, reaction conditions, detention times and catalyst concentrations.

CONTACTING METHODS

A method of contacting lagoon sediments with the active agents in a conversion process must also be selected prior to the development of an alternative. Three contacting schemes are proposed for desensitization. These are designated as insitu solid phase (solid phase in the lagoon); insitu liquid phase (liquid/lagoon) and liquid phase as a sidestream in an adjacent reaction vessel (liquid/sidestream).

Solid phase contacting is proposed as a means to attain the insitu treatment of the undisturbed sediment by permeation of liquid or gaseous reagents through the sediments to promote contact with the explosives. There is no mixing, dilution or excavation of the sediment. The solid

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phase contacting is confined to chemical injection techniques. It is essential that the sediments have been deposited within a lined lagoon or be underlain by an impermeable soil strata, otherwise the chemicals may contaminate underlying groundwater.

The major advantages of solid phase contacting are:

o   Minimizes handling and safety problems

o   Accommodates long retention times (repeated passes)

o   Supports the insitu stabilization of sediments and closure of the lagoon

The major disadvantages of solid phase contacting are:

o   Applicable only for permeable sediments in which there is a relatively uniform distribution of explosives

o   Applicable only for chemical injection techniques

o   Limited to ambient temperature

o   The end products or the reagents themselves may be toxic or catalyze the release of toxic compounds

o   Excess reactant concentrations are required to minimize the risk of inadequate or incomplete conversion

Liquid phase contacting in the lagoon involves the insitu resuspension, dilution and reaction of the lagoon sediment. There is assumed to be no removal of sediment from the lagoon until after desensitization is achieved, such that the lagoon is operated analogously to a batch reactor. Liquid/lagoon contacting is applicable for some of the chemical and biological conversion processes.

The advantages of liquid/lagoon contacting are:

o   Minimizes handling and safety problems (although more handling is required than for solid phase contacting)

o   Accommodates long retention times

o   Supports insitu stabilization of sediments and closure of the lagoon

o   Permits good contacting of sediments with desensitizing agents

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The disadvantages of liquid/lagoon contacting are:

o   Expansion of lagoon volume and dilution of the sediments may be required, with attendant need to elevate berms and containment dikes

o   Limited to ambient temperature

o   The end products or the reagents themselves may be toxic or catalyze the release of toxic compounds

Liquid phase contacting as a sidestream in an adjacent basin may or may not require extensive dilution of the sediments after resuspension, the primary requirement being that the sediment can be hydraulically excavated and transferred from the lagoon to a holding tank or reaction vessel prior to the desensitization treatment. When a holding tank is used, the sediment can be transferred from the holding tank for treatment on a continuous-flow process alternately, the sediment can be treated batchwise in sequenced batch reactors.

The advantages of liquid/sidestream contacting are:

o   Facilitates the separation and concentration of solids as well as the chemical or biological conversion

o   Permits better process control and continuous-flow operation

o   Allows the reaction temperature to be adjusted

o   Permits good contacting of sediments with desensitizing agents

o   Is applicable for all conversion processes

The disadvantages of liquid/sidestream contacting are:

o   Limited to shorter retention times

o   Requires more handling of the sediments, thereby increasing handling and safety requirements

o   Maximizes equipment requirements

o   Increases the complexity of the desensitization system (maintenance and operating requirements)

PERFORMANCE MEASURES

Performance measures are used to evaluate the feasible alternatives objectively and subjectively as to preference for the lagoon being treated. If necessary, these factors can be weighted at any one site to emphasize a desirable situation. An example of such a situation would be the compatibility of the desensitization facility with an existing facility for the treatment of the liquid effluent. Alternatives can be rated by comparison for a high, moderate, or low impact on each performance measure unless numerical measures are appropriate. The performance measures used to compare alternatives in this report are flexibility, degree of desensitization, implementation time, complexity, risk acceptability, state-of-the-art, cost and disposability. Definitions of these specific measures, selected for purposes of this report only, are presented below.

Flexibility

This parameter indicates the suitability of the alternative for treating the various explosives present in the sediment. A high rating indicates that the alternative is applicable to all explosives.

Degree of Desensitization

Although acceptable levels are yet to be defined, the degree of desensitization achieved is related to either the technology or the threshold at which risk is acceptable, whichever is greater. An increasing degree of desensitization is indicated (subsequently, in Chapter 6) by a higher rating.

Implementation Time

This measure evaluates the overall time requirement for the implementation of the alternative. Implementation time is equal to the sum of mobilization, processing, and demobilization time. A rating of high is indicative of a mobile and time-efficient alternative.

Complexity

Complexity is a subjective measure related to operating and maintenance requirements. A high rating is indicative that a large amount of downtime is expected, and high operator skill and maintenance are required.

Risk Acceptability

This is an aggregate measure of the safety hazards to personnel at each step, cumulated through the alternative. Examples of safety hazards are radiation exposure, flash point, toxic fumes and reactivity. A low rating is indicative of a minimum amount of safety hazards.

State-of-the-Art

This is a measure of the development status of the alternative. Existing on-line technology with a record of satisfactory performance is indicated by a high rating; technology that has only a theoretical basis or has been demonstrated by only a few laboratory studies is given a low rating.

Cost

The estimated capital and operating costs for each alternative are rated by comparison.

Disposability

Disposability is an objective measure of the environmental risk and impact of products and byproducts of desensitization. The form, toxicity and mobility of the compounds produced are taken into consideration. A disposability rating of high indicates that the products and byproducts of desensitization are expected to have a minimal environmental impact.

SAFETY REQUIREMENTS

Safety planning addresses issues necessary to protect people and equipment during handling, processing, and disposal operations. Although safety is an integral element of the approach to desensitization, at the conceptual level it was only possible to assume that appropriate measures can be implemented without limiting the feasibility of any proposed approach. The true dimensions of safety requirements cannot be envisioned until a more detailed approach including laboratory and pilot scale operations is developed.

CHAPTER 3

DESENSITIZATION TECHNOLOGY

The essential elements of desensitization technology are divided into the following categories: initial materials handling, secondary materials handling, conversion processes, and separation processes. Initial materials handling is defined as the series of steps or operations needed to initiate the desensitization process. Secondary materials handling includes the storage, transfer and blending operations necessary to prepare the sediment for desensitization. Conversion processes are those chemical, thermal or biological transformations in which desensitization occurs. Separation processes are used to divide materials into their solid and liquid fractions and can be used with lagoon sediment and the products or byproducts of desensitization.

The elements of technology identified in the literature search were reviewed and evaluated for applicability as unit operations and processes for desensitization. Major emphasis was placed upon the conversion processes. Emphasis was also placed upon initial materials handling because this is an essential part of any desensitization concept. Secondary materials handling operations are essentially ancillary in nature and were not evaluated. Separation processes are described by class only as this technology is applied primarily to desensitized material.

INITIAL MATERIALS HANDLING

Three classes of technologies were considered for initial materials handling: injection/recovery, hydraulic resuspension and hydraulic excavation. One or more of these technologies will be required for each alternative. All technologies will require developmental work since none are proven for this application.

Injection/Recovery

Injection/recovery has as its prototype the technology of solution

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leaching, a process in which chemical solutions are injected below the
surface into an ore body, circulated and then recovered at the surface.
Ore, solubilized during this process, is extracted from the solution.
Solution leaching is a relatively new process currently under development
by the U.S. Bureau of Mines. Approximately 25 uranium mining and four
copper mining pilot projects were reported for solution leaching as of 1979
(Kasper, et al, 1979). Technology for this process is still in the
developmental stage.

The suitability of a site for solution mining is determined by the
characteristics of the ore body and hydrologic considerations. Preliminary
studies are conducted to determine the geometry and extent of the ore body.
The porosity, permeability, hydraulic gradient and natural groundwater
movement of the ore zone are also determined. The data obtained from the
hydrologic survey are used to develop an injection-extraction well layout.
An appropriate well layout is required for uniform solution distribution
and containment; a typical pattern consists of injection and recovery wells
installed at spacings varying from 25-100 feet. The production wells are
surrounded by a ring of monitoring wells to ensure protection of the
aquifer. If traces of the leaching solution are detected in a monitor
well, the rate of recovery can be increased or the rate of injection
decreased to control the distribution pattern.

A vertical cross-section of a typical solution leaching layout is
shown in Figure 3. The well points can be driven into the sediments by
hydraulic jet. Polyvinyl chloride (PVC) pipe is normally used for casing.
The above-ground equipment consists of an injection pump, a storage/mixing
tank for chemicals and a pipe network for connecting the well points to the
processing plant.

Applicability to Lagoon Sediment

The deep well insitu mining technique is not directly applicable to
treatment of lagoon sediments because of their proximity to the surface and
relatively shallow depth. High pressure (50 psi) cannot be used for well
development or chemical injection because "blowouts" would occur in the

FIGURE 3. VERTICAL CROSS SECTION OF TYPICAL IN SITU SOLUTION LEACHING LAYOUT
FOR URANIUM ROLL FRONT DEPOSIT (KASPER, et al., 1978)
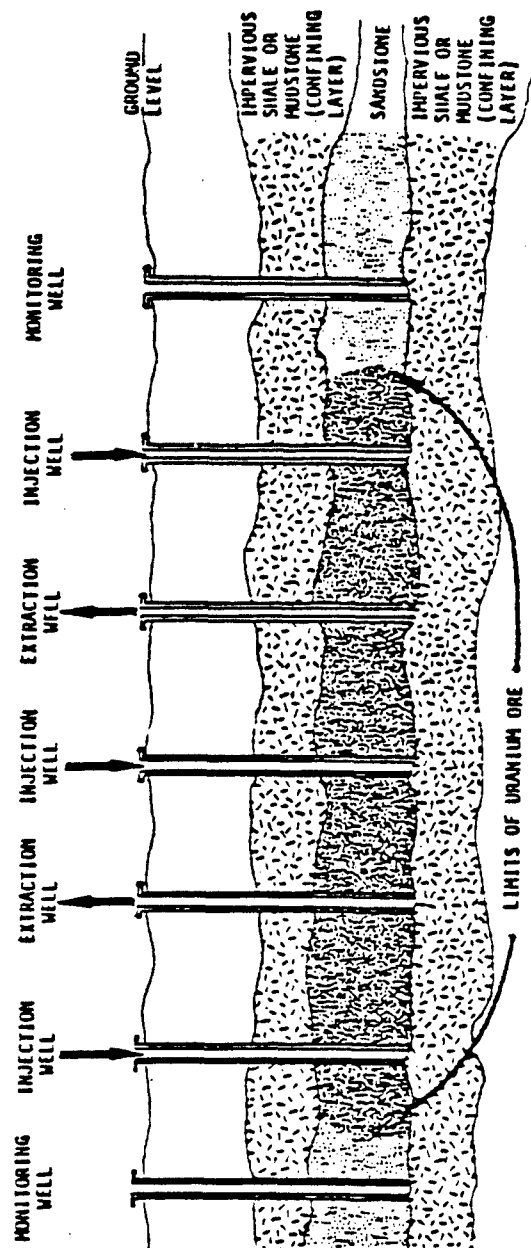
immediate vicinity of each well point. Therefore, a modification to the insitu mining technique is proposed for lagoon sediments. The alternative, shown in Figure 4, consists of the installation of a well point system with alternate injection/withdraw points oriented in rows. To preclude the release of materials from the vicinity of the lagoon, all outer well points are used for withdrawal. It is anticipated that this system would be used in combination with surface flooding and that well points could be installed hydraulically from a floating platform. Alternatively, a distribution piping system could be placed on the lagoon bottom to facilitate chemical injection. The system could be installed in narrow channels in the sediment.

Factors affecting the feasibility of these techniques are sediment permeability, distribution of explosives, depth of sediments, underlying geology and the degree of desensitization required. Saturated flow conditions must be achieved for this approach to be feasible; unsaturated flow (sandbeds) would result in poor distribution (short circuiting). An ideal lagoon for this approach would consist of a uniformly distributed permeable sediment developed over an impermeable lagoon bottom (natural clay or liner). The potential problems with this approach include the precautions needed to install the well points in shallow sediments so as to not disturb the underlying impermeable layer, and the development of a sufficient hydraulic gradient through the sediment.

Injection/recovery techniques should minimize materials handling and safety requirements by eliminating the need to excavate or resuspend lagoon sediments. In addition, this technology would be advantageous if insitu stabilization and lagoon closure are the preferred approach to remediation.

Cost Factors

The major costs for this technology are incurred for the installation of well points and the injection/recovery pumping system. The actual cost would be dependent upon the number of well points and volume of pumping, piping, solution holding/mixing tanks and utilities required which in turn would be dependent upon the lagoon characteristics.

FIGURE 4. COMBINED SURFACE FLOODING/INJECTION RECOVERY TECHNIQUE
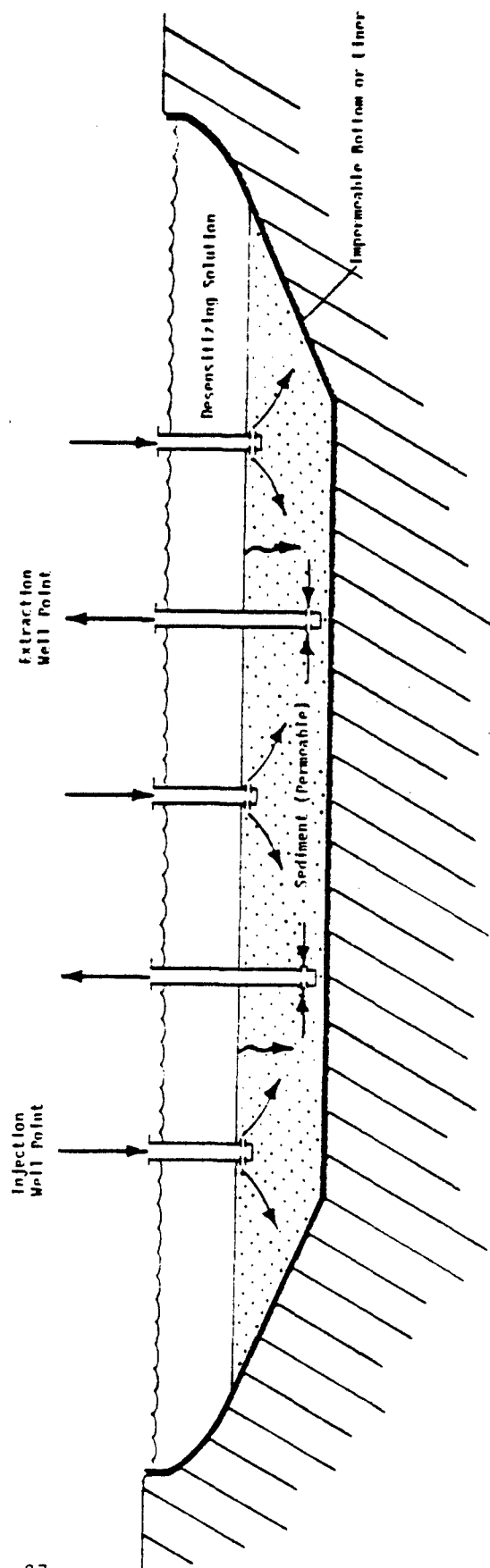
Environmental Impact

The primary environmental concern would be the potential for migration of the desensitizing solution, the products or the byproducts to the surrounding groundwater. Monitoring wells would have to be used to detect any releases. The total system should be designed for maximum recovery and reuse of desensitizing solution either at the same or another site.

Hydraulic Resuspension/Excavation

Hydraulic resuspension/excavation techniques are considered together for discussion purposes due to the similarity of the operations and equipment involved. Hydraulic resuspension techniques are used to slurry the lagoon sediment. Progressively increasing portions of the lagoon can be placed and maintained in suspension until the entire lagoon is resuspended or portions of the lagoon may be taken out of suspension as other portions are suspended. Excavation techniques are used to remove sediment from the lagoon; excavated with or without much dilution and resuspension. Two existing technologies are proposed for suspension/excavation: borehole slurrying and dredging.

Hydraulic Borehole Slurrying

The hydraulic borehole slurrying technique, illustrated in Figure 5, has recently been proposed and demonstrated for insitu mining. The first step consists of drilling a borehole into the ore zone. Ore is then slurried by a rotating water-jet cutting device lowered into the borehole, and the slurry is returned to the surface by a submersible pump. Solubilized ore is then extracted from the recovered slurry (Kasper, et al, 1979).

The water jet device is contained within an assembly which is lowered into the borehole. The cutting jet is at the end of a rigid service column which contains the necessary piping for pressurized water transfer and slurry recovery. The lower section of the assembly contains the submersible slurry pump. The above-ground equipment includes pumps, tanks and separators.

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FIGURE 5. SCHEMATIC DIAGRAM OF THE HYDRAULIC BOREHOLE SLURRY
MINING TECHNIQUE (KASPER, et al., 1979)
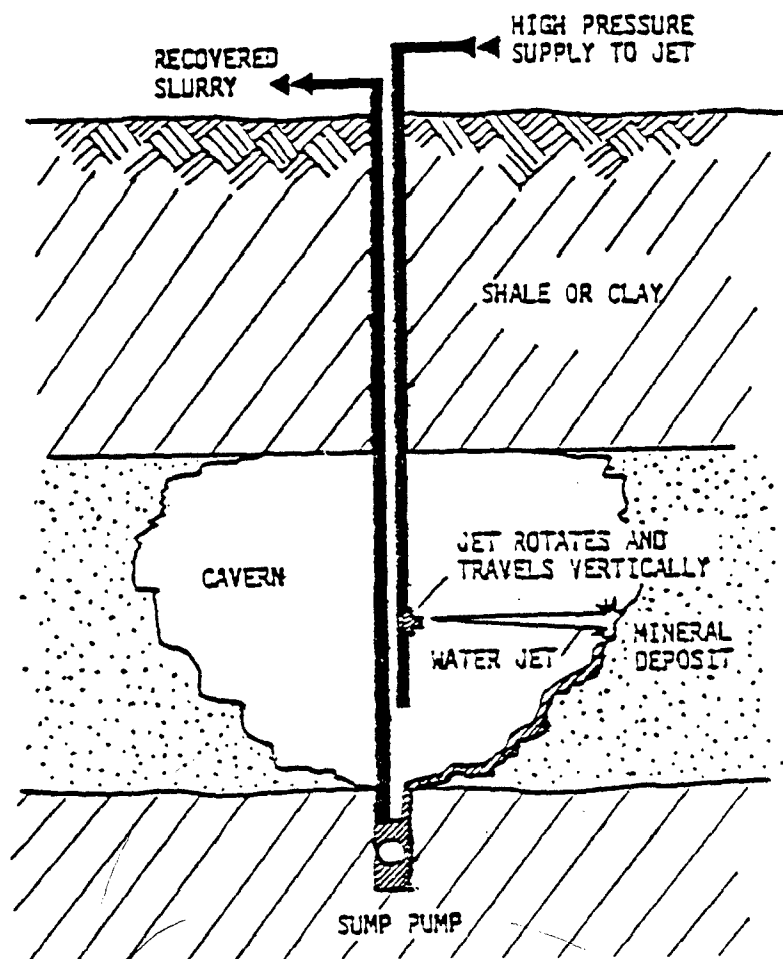
Dredging

Dredging is a widely utilized procedure for the underwater excavation of material. Specialized dredges are available for the various types of materials (sand to hard rock) and operations (depth and extent of area) encountered. Suction dredges are the most widely used type. The size of the dredge is determined by the amount and type of material to be moved and the desired production rate. A cutter head may also be required when the material requires loosening or fracturing.

A horizontal auger dredge, manufactured by the Mudcat Division of National Car Rental, has been demonstrated to be effective for the removal of hazardous material from pond bottoms. During an EPA-sponsored study (Nawrocki, 1976), four different simulated hazardous materials (very fine iron powder, fine glass beads, iron filings, and coal) were placed on the pond bottom. These materials were then removed by the Mudcat dredge. Subsequent testing determined that the removal efficiency of the dredge was an average of 99.3 percent for all four materials. An additional test using an actual hazardous material, latex paint, was conducted, during which the dredge removed 95.5 percent of the paint pigment.

Mudcat was contacted for information on the horizontal auger dredge. The Mudcat Model SP-810, shown schematically in Figure 6, was recommended for this application. This dredge is designed for processing materials having a high solids concentration and includes a hydraulically driven submersible pump mounted on the end of a boom directly behind the auger. The dredge must be lowered into the lagoon by crane. Dredge movement, illustrated in Figure 7, is controlled precisely by means of a cable winching arrangement. During processing, the dredge operator winches back and forth on a fixed-traverse cable dead-manned on both ends of the lagoon. The dredge also contains a calibrated mechanical depth gauge enabling the operator to know the exact vertical position of the auger below the lagoon surface level. Once the desired depth is reached, the boom is raised and both ends of the traverse cable are moved equal distances and repositioned parallel to the previous cut. A one-foot overlap is normally maintained. Excavated material can be returned directly to the lagoon or discharged to shore via a floating pipeline.

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FIGURE 8. MUDCAT MODEL SP-810 DREDGE (MUDCAT, 1982)

FIGURE 7. DREDGE CABLE-WINCHING ARRANGEMENT (MUDCAT, 1982)

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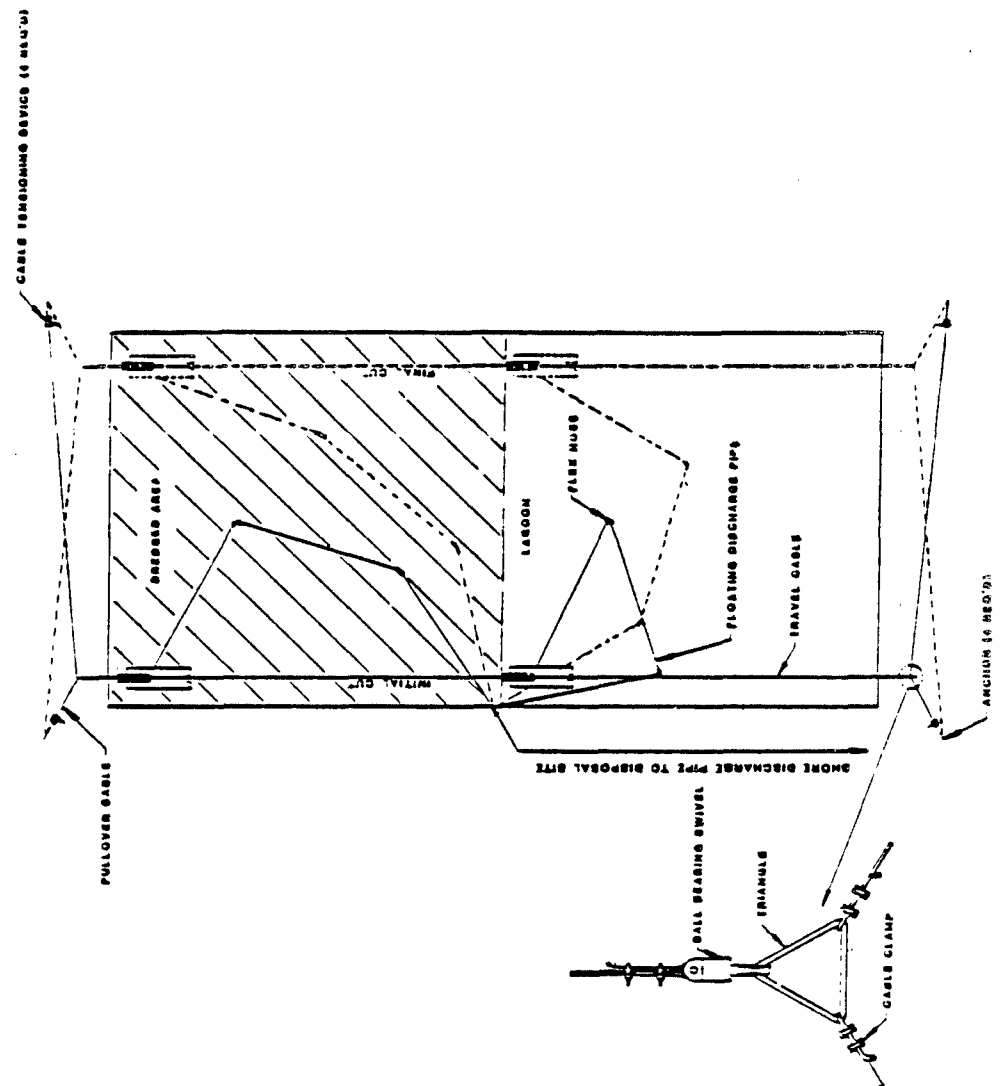
The auger assembly utilizes cutte. knives to dislodge solid material
and a spiral auger to drive the material into the pump. An optional auger
cage assembly (Figure 8) is available for operation in a lined lagoon. The
horizontal bars of the cage assembly prevent the auger from coming into
contact with the lagoon liner. Hydraulic cutting jets can also be attached
to the auger assembly. The principal controls for the dredge are operated
hydraulically from the dredge cabin. Remote control operation is feasible;
for example, three radio-controlled dredges have been ordered by the U.S.
Steel Corporation (Shenman, 1982).

Applicability to Lagoon Sediment

Dredging is a proven technology for the excavation of lagoon sediment.
Only small equipment and operating modifications are anticipated for this
application. If it is feasible to adjust the water level in a lagoon above
the surface of the sediments, the necessary volume of water would be added
to the lagoon prior to dredging. The dredge would then be lowered into the
lagoon and operated using the cable-winching arrangement for control of
movement. An auger cage and hydraulic jets may be required to minimize the
possibility of damage from tramp metals and large objects, and to prevent
liner damage. Safety considerations may also warrant the additional costs
of equipping the dredge for remote-controlled operation and/or metal
detection.

The solids content of the dredged suspension will be dictated by the
characteristics of the lagoon and the proposed conversion process. For
some conversion processes it will be advantageous to excavate the sediment
with minimal dilution. The maximum allowable solids concentration for
hydraulic excavation will be determined by the characteristics of the
sediments. A minimum of 21 inches of water must be available to float the
dredge. If necessary a narrow operating channel can be cut into the lagoon
and filled with water to allow initial dredging. Additional water can then
be added as the hydraulic jets cut into the sediment.

Borehole slurrying techniques can be adapted for hydraulic contacting
of lagoon sediment with desensitizing solutions. In such a case the

FIGURE 8. AUGER CAGE ASSEMBLY (MUDCAT, 1982)
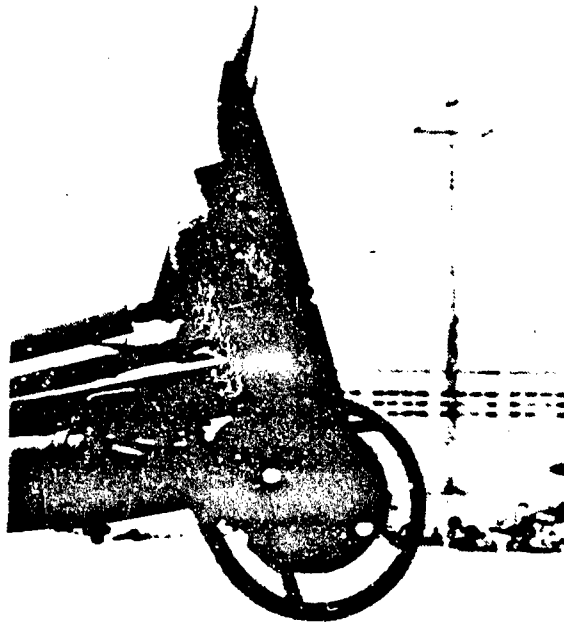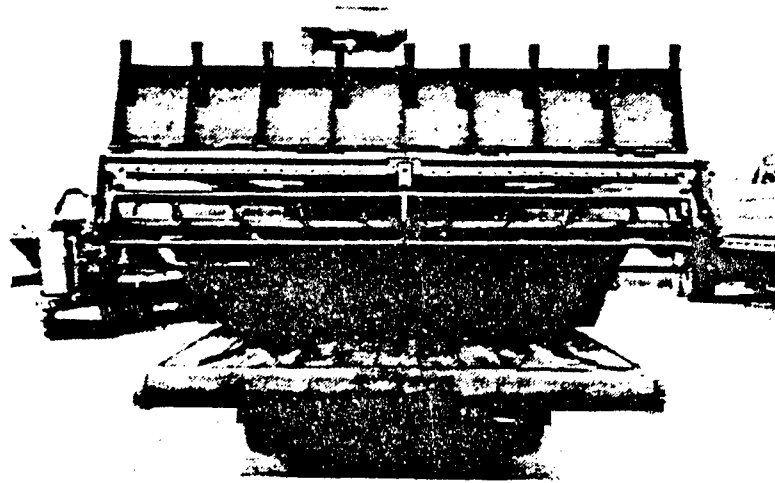
hydraulic cutting jets would have to be mounted for both transverse and vertical movement across and within the lagoon. A desensitizing solution would be used to slurry and suspend the sediments for contacting purposes. The suspension would not be maintained, but rather allowed to resettle as the cutting jet assembly is moved to a new position. This "localized fluidized bed" effect would allow intimate contacting between the sediment and desensitizing solution without the need to maintain the entire sediment inventory in suspension. Unreacted desensitizing solution would be reused as the cutting jet assembly is moved. As with the dredging operation, a cable-winch arrangement would be used to control the movement of the cutting jet assembly.

Both the modified dredging and slurrying techniques appear feasible for treatment of lagoon sediments. These techniques are intended to illustrate the types of material handling techniques that appear to be feasible, although both may require modification and development.

Cost Factors

The cost of hydraulic resuspension/excavation by either process would again be site-specific. The processing rate is dependent upon the degree of dilution or solids concentration, lagoon shape (maneuvering requirements) and size and depth of contamination.

The primary costs for hydraulic slurrying are associated with the water jet cutting assembly, pump systems and holding tanks, piping and utilities. The major cost for the dredging system will be for the rental or purchase of the dredge package (including the dredge, piping, cable-winch and harness), crane rental and diesel fuel.

Environmental Impact

The major environmental impact of hydraulic resuspension/excavation will be with respect to the groundwater. The lagoon bottom must be impermeable, and monitoring wells should be installed to detect the release of any chemicals.

SECONDARY MATERIALS HANDLING

Secondary materials handling pertains to the storage, transfer and blending operations necessary to prepare the sediment for desensitization. Typical secondary materials handling operations are maintaining lagoon sediments in suspension, slurry transfer, slurry dilution, solids transfers and slurry holding. The reactivity of the sediment will also necessitate the development of safety procedures for secondary materials handling operations.

SEPARATION PROCESSES

Solid-liquid separation is expected to be an optional or required process for most desensitization alternatives. Gravity sedimentation is expected to be used most commonly and specialized gravity systems such as hydraulic classifiers may be cost-effective in some alternatives (e.g., incineration). Processes such as dissolved air flotation, filtration and centrifugation may also be required in a treatment train. The characteristics of the suspension will be a primary determinant of the type of separator selected. The added cost of an easily transportable process may offset any additional capital costs of that process. Also, the reactivity of the material being processed will also determine the choice of equipment.

Separation processes such as ion-exchange and carbon adsorption may also be required for concentration and recovery/disposal of unreacted chemicals or toxic substances. The selection of these processes is subject to the same considerations as the solid-liquid separation processes and selections should not be made until lagoon characterization and laboratory/pilot treatability studies have been performed for the selected alternatives.

CHEMICAL CONVERSION PROCESSES

The chemical reactions for desensitization of explosives can be classified as radiative, reduction, oxidation, complexing, hydrolysis and

decomposition. Conversion processes within each category were evaluated for their adaptability for the treatment of lagoon sediments based upon a review of the literature. Several processes were identified for further consideration: chemical reduction, gamma irradiation, surfactant complexing, hydrolysis and alkaline digestion. Of these, surfactant complexing and hydrolysis were considered as a single treatment process due to the similarity of reaction conditions and synergistic effects. These processes and their applicability to desensitization are described later in this section.

The literature was also reviewed on the use of hypochlorites, acids and several proprietary decontamination solutions for desensitization by oxidation. A large portion of the literature was concerned with decontamination to eliminate trace amounts of explosives. Studies performed using hypochlorites (sodium or calcium) were primarily concerned with color removal. The large dosages, high free chlorine residuals reported and corrosive properties of hypochlorites combine to make desensitization by chlorination unattractive (Edwards and Ingram, 1955; Stuart, et al, 1943). The use of proprietary decontamination solutions, hypochlorite or carbonate is undocumented for the desensitization application and would most likely not be cost-effective. In addition, sodium carbonate is reported to react with TNT forming a compound that is as sensitive to heat and impact as is tetryl (Army Technical Manual, 1967). TNT like other nitro aromatic compounds is resistant to oxidation by acids. Only concentrated acids at elevated temperatures (110-200°C) can oxidize TNT (Urbanski, 1964).

Little information is available on the oxidation of explosives by peroxides and peroxide systems. However, the use of Fenton's reagent which is a mixture of aqueous ferrous sulfate and hydrogen peroxide, has been reported to be effective in the oxidation of nitro aromatics (Urbanski, 1964). Although not evaluated in detail, this system will be further described later in this chapter.)

In a study performed by General Electric it was found that ozonation caused only a small reduction in the concentration of pure TNT in

solutions. Ozonation experiments performed on single-component solutions of RDX and HMX failed to reduce the concentrations of these explosives (Jain, 1976). It was concluded that simple ozonation was "grossly inadequate in removing any of the three materials." However, the reactivity of each material to ozone was greatly enhanced by simultaneous irradiation of the material with ultraviolet (UV) light (Jain, 1976). For the reasons cited above, the oxidation reactions evaluated were judged infeasible for desensitization.

The photochemical degradation of explosives by UV irradiation has been investigated by a number of researchers. The synergistic effect of UV irradiation and oxidants (ozone, peroxides) is well documented (Jain, 1976; Andrews, 1980). Although this process has been used on a pilot scale for the treatment of pink waters (Layne, et al, 1982), its applicability to treatment of lagoon sediments is questionable. For photochemical degradation to be effective, the light itself must reach the explosive molecule. This is normally accomplished by placing the explosive in an aqueous solution that contains little or no suspended solids. Due to the low solubilities of the explosive compounds considered in this study (e.g., 130 mg/l of TNT @ 20°C, and 76 mg/l of RDX @ 25°C), a tremendous volume of dilution water would be required for each lagoon. The large volume of dilution water could entail significant material handling costs and necessitate large scale treatment units. In addition the presence of sediments and other materials in solution would attenuate the light by adsorption and scattering.

The desensitization of explosive-laden lagoon sediment by UV-oxidant has been evaluated by the Atlantic Research Corporation (ARC) (Wentsel, et al, 1981). The proposed process involved dilution of the sediment to solubilize all explosives, the degradation of the explosives into biologically treatable compounds and biological treatment. The estimated capital and annual operating costs of this unproven technology were $9,500,000 and $3,800,000 per year in 1981 dollars. These costs in combination with the aforementioned problems make the feasibility of the UV-oxidant process questionable.

Chemical Reduction

Explosives and propellants can be generally classified as oxidants. The addition of reductants to these compounds can result in a chemical reaction which converts the oxidants to a less sensitive form. TNT, RDX, HMX, tetryl, nitroglycerin, nitroguandine, and nitrocellulose are explosives and propellants which comprise a group of organic compounds sharing in common the presence of one or several nitro groups. Nitro groups in some explosives are reduced to amino groups by the substitution of hydrogen for oxygen present in the group. The compound containing the amino group is much less sensitive than is its original form. It may only be necessary to convert one of several nitro groups present to accomplish the desensitization of the compound. Nitro groups in other explosives are not converted but, instead, are substituted by hydrogen. In this manner the explosives are returned to their original compounds prior to nitration. Hydrogen is supplied to the compound by a reducing agent or reductant. The reductant can be acidic or alkaline, and added at ambient or elevated temperature, in aqueous or non-aqueous solution, or in solid or gaseous form.

Reductants can be broadly classified into inorganic and organic compounds. The inorganic category includes the sulfur-containing compounds; sodium sulfide, sodium bisulfide and sodium metabisulfide; and the non-sulfur containing compounds; hydrazine and sodium borohydride. The organic category includes the carboxylic acids (such as formic and oxalic acids), the hydroxyl acids (such as citric and tartaric acids), glucose (a reducing sugar) and gases (such as methane and carbon monoxide). Reductants can be chosen so that only the elements contained in the original explosive are present in the reductant; in this manner no new pollutants are introduced into the material. This approach is particularly useful when the final material is incinerated (Roth, 1978).

Theory

In order to evaluate the effectiveness of a reductant, it is first necessary to understand the oxidation-reduction reaction. Oxidation and

reduction can be defined on the basis of change in oxidation number. Oxidation is a process which results in an algebraic increase in the oxidation number and reduction results in an algebraic decrease. The total increase in oxidation number of one species must equal the total decrease in the oxidation number of another species. The equivalent weight system for oxidizing and reducing agents is based upon the change in oxidation number. The equivalent weight of a compound functioning as an oxidizing or reducing agent is defined as the molecular weight of the compound divided by the total change in oxidation number of all atoms in one formula weight of that compound. One-gram equivalent weight of an oxidizing compound requires one-gram equivalent weight of a reducing compound for complete reaction. Therefore, the use of a reductant which contains a low equivalent weight and/or several equivalent weights per mole is preferred to the use of a reductant which has a high equivalent weight and/or only one equivalent weight per mole.

The effectiveness of the reductant in this type of oxidation reaction can also be evaluated from the standpoint of available hydrogen. In general, the reductant releases hydrogen (directly or indirectly after hydrolysis in water) and the oxidant accepts hydrogen. A reductant with several available hydrogen atoms per mole is more effective than a reductant with only one available hydrogen atom per mole.

The reduction of a nitro group to an intermediate nitroso group and then to the final amino group is illustrated below:

$$R-NO_2 \quad \xrightarrow{\text{Reductant}} \quad R-NO + H_2O$$

$$R-NO \quad \xrightarrow{\text{Reductant}} \quad R-NHOH$$

$$R-NHOH \quad \xrightarrow{\text{Reductant}} \quad R-NH_2$$
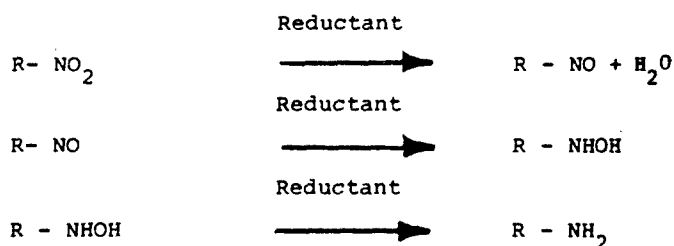
The final form of the reduced compound and the byproducts of the reduction are dependent upon the reductant used, the reaction conditions and the degree of desensitization achieved. Figure 9 is a summary of

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FIGURE 8. SULFUR-BASED REDUCTIONS OF EXPLOSIVES (MEZEY, et al., 1982)

APPLICABLE EXPLOSIVES AND REACTIONS:

NG $\xrightarrow[\text{Na}_2\text{S}]{\text{NaHS}}$ glycerol + NH_3

NC $\xrightarrow[\text{Na}_2\text{S}]{\text{NaHS}}$ cellulose + NO_x + H_2S + NO_2^-

TNT $\xrightarrow{\text{Na}_2\text{S}}$

RDX, HMX $\xrightarrow[\text{Na}_2\text{S}_2\text{O}_3]{\text{Na}_2\text{S or}}$ $-N-NH_2$

Tetryl $\xrightarrow[\text{Na}_2\text{S}_2\text{O}_3]{\text{Na}_2\text{S or}}$ non-explosive, water soluble products

NGu $\xrightarrow[\text{pH 11}]{\text{Na}_2\text{S}}$ $NH_2-\overset{NH}{\overset{\|}{C}}-NHNH_2$

41
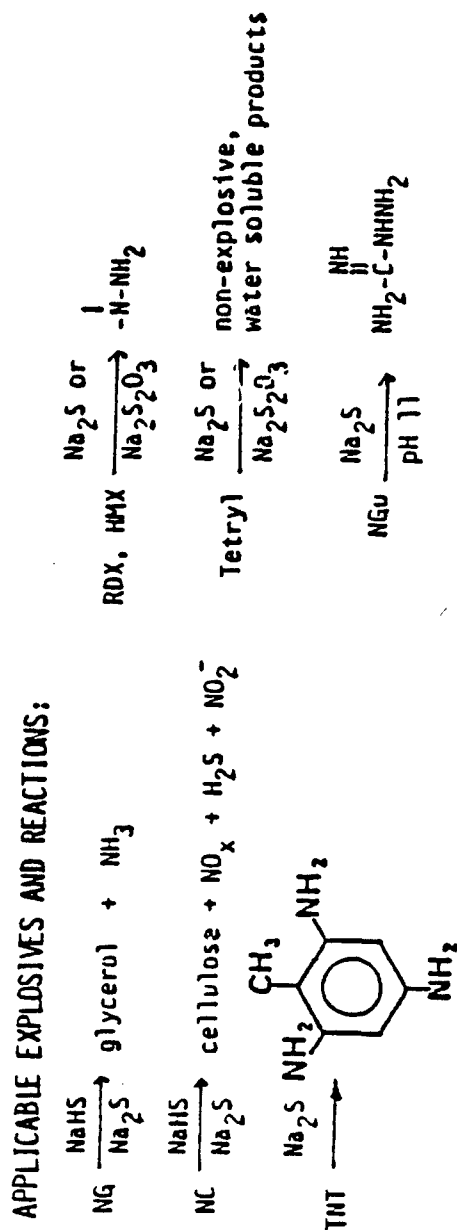
generalized reactions anticipated for the explosives and propellants using sulfur-based reductants. The reactions illustrate the diversity of organic byproducts and end products that can be expected. For example, nitro-glycerin and nitrocellulose yield glycerol and cellulose respectively when reduced while other explosives such as TNT, RDX and HMX yield products containing amines.

Prior Experience

Several feasibility studies have been performed under contract to the Army to identify appropriate reductants for desensitization (Roth, 1978; Army ARDC, 1981). As a guidepost for this effort the Army defined as a preferred reductant a compound that is: (1) composed of the same elements as the explosive; (2) non-toxic; (3) highly soluble in aqueous solution and (4) low in cost. Sodium sulfide, which is the reductant of choice for laboratory use (Engineering Design Handbook, AMCP 706-177), was identified as the standard reductant; however, it was not considered for large scale use due to its undesirable odor and toxicity characteristics. The feasibility testing was performed by adding dried samples of TNT or RDX to aqueous solutions of reductants at varying concentrations. For the conditions tested, hydrazine, citric acid, oxalic acid, formic acid, ascorbic acid and tartaric acid were identified as t˙   st effective reductants. These reductants were very successful foi ·eating TNT but less so for RDX. As is predictable theoretically, the reductants with several equivalent weights per mole (such as hydrazine and sodium sulfide) were more effective than reductants containing only one equivalent weight per mole (such as formic acid) when applied at the same molarity.

Based on test results, ascorbic acid was eliminated from consideration due to its high cost, low solubility and questionable shelf life. A further recommendation was that selection of the optimum treatment conditions be delayed until more definitive data were developed for the treatment of RDX.

A detailed test plan was proposed for this purpose but the tests were never performed. There was no information available in the literature on the reaction products or byproducts.

Hydrazine-hydrate was used to reduce nitrocellulose in laboratory feasibility studies conducted at the Natick Research Laboratories (Bissett and Levasseur, 1976). The study found that nitro groups bonded to the cellulose could be removed without destroying the cellulose. A nearly quantitative yield of cellulose was obtained as a precipitate when the nitrocellulose was dissolved in tetrahydrofuran prior to being reacted with hydrazine-hydrate. When the reaction was performed in the aqueous phase, approximately 50 percent of the cellulose was retained in solution. It was suggested that the hydrazine may become bonded to cellulose during an aqueous phase reaction.

Applicability to Lagoon Sediments

Based upon prior experience, chemical reduction is a viable alternative for desensitization of explosives contained in lagoon sediments. The conversion processes in this category can be used to treat all the explosives and propellants expected in the lagoon sediments. Chemical reduction is applicable to each of the three contacting methods; solid-phase, liquid/lagoon and liquid/sidestream, as discussed earlier. Reductant solutions (aqueous or organic) can be injected into the solid phase, recovered and either recirculated directly or treated for disposal or reuse. Reductant solutions can also be used as a medium for slurrying the sediment or can be added in solid form to a slurry. Depending upon the choice of reductant, direct reuse, neutralization or concentration/reuse of the reductant may be appropriate.

The large variation in the characteristics of a lagoon allows considerable latitude in the choice of reductants. For example, the use of sodium sulfide may be feasible under highly controllable conditions. Sodium sulfide is relatively inexpensive, highly effective and has been used successfully to treat plating shop wastewaters. The use of hydrazine, if practicable, is also desirable due to its low molecular weight and four reducing equivalent weights per mole.

Desensitization alternatives using chemical reduction are flexible and easily integrated into a treatment concept. Pretreatment by chemical

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reduction could result in the generation of a residual solids stream of lower moisture content; advantageous in a system involving incineration. Also, the toxic characteristics of reductants such as sodium sulfide and hydrazine are less significant if incineration or stabilization is a final treatment method. An insitu chemical reduction using a reductant in either solid or liquid form would eliminate unnecessary materials handling operations. In cases such as liquid-phase biological treatment after desensitization, the added cost of a non-toxic reductant may be more than offset by an overall savings in avoiding the later elimination of a toxic effect.

Cost Factors

The equipment costs of these alternatives will vary with the selected initial material handling and desensitization alternatives. The chemical dosage requirements are a function of the type and concentrations of explosive and of competing chemical demand if such is present. The degree of desensitization required by the overall approach will also affect the chemical requirements, i.e., more chemical reductant will be required for 99 as opposed to 90 percent desensitization. The choice of reductant impacts upon both chemical and equipment costs; reductants such as sodium sulfide require neutralization (e.g.,with hydrogen peroxide) prior to discharge, but other reductants can be concentrated for recovery (e.g., oxalic acid by lime precipitation). The optimum dosage, operating conditions and post treatment requirements will be site specific.

Environmental Impact

The environmental impact of the chemical reduction processes will depend upon the choice of reductants, the reaction conditions and the type and concentration of explosives and other compounds present in the sediment. The use of sodium sulfide would require a closed mixing system, a closed reactor and hydrogen sulfide gas monitors. Monitoring wells would be necessary for any insitu contacting method.

Very little information is available on the reaction products and byproducts for the chemical reduction of explosives. The limited amount of

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information is based upon reductions occurring with neat explosives in pure reductant solutions. For example it is known that toxic amines are formed from the reduction of nitroaromatics with sulfur-based compounds. However, the effect of these reductants and any corresponding change in the character of the slurry (e.g., its pH) on other compounds in the lagoon sediment is undefined as are the types of reduction products and byproducts from the reductants.

Complexing-Hydrolysis

Amino surfactants at alkaline pH have been found to precipitate TNT as a water-insoluble complex. Although RDX, HMX and nitroglycerin are not precipitated, the hydrolysis of these compounds is accelerated under alkaline conditions by the surfactant. Studies have been performed with these explosives in solutions and also of the insitu immobilization of TNT with surfactants in contaminated soils. The mutagenicity, decomposition and soil leaching properites of the TNT-surfactant complex have also been investigated.

Theory

Two types of surfactants containing amino groups have been identified as effective in the precipitation of TNT from solution. One of the surfactants contains a primary amine as the polar group and the other a quaternary amine. The TNT reacts with amine in aqueous solution to form 2,4,6 -Trinitrobenzyl anion (TNT). The TNT anion reacts with TNT to form the Janovsky complex. The complex then reacts with the protonated surfactant and is precipitated as a salt (Okamoto, et al, 1973).

The alkaline hydrolysis of RDX, HMX and nitroglycerin is greatly accelerated by the presence of a cationic surfactant (Okamoto, et al, 1973). The increased rate is most likely due to the solubilization of the explosive by the surfactant micelles (Freeman and Colitti, 1982). The rate of hydrolysis of RDX was increased 75-fold while the rate of HMX hydrolysis was increased 25-fold by the presence of the surfactant. The appropriate reactions are shown in Figure 10 for TNT, RDX and nitrocellulose.

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FIGURE 10. COMPLEXING-HYDROLYSIS REACTIONS (FREEMAN, COLITTI, 1982)

TNT: SURFACTANT-COMPLEX FORMATION

For the reaction of TNT with the cationic surfactant - NaOH system, the complex formations may be illustrated as follows:

$$Surfactant (R_4N^+ Cl^-) + NaOH \rightleftharpoons R_4N^+OH^- + NaCl$$

$$TNT + R_4N^+ OH^- \longrightarrow TNT^- R_4N^+ + H_2O$$

$$TNT^- + TNT \longrightarrow (TNT^-)(TNT)$$
$$Janovsky \ complex$$

$$(TNT^-)(TNT) + R_4N^+ \longrightarrow (TNT^-)(TNT) R_4N^+$$
$$precipitated$$

RDX: HYDROLYSIS

$$decomposed \ to$$

$$\xrightarrow{k_2} CH_2O, \ HCOO^-, \ N_2O, \ NH_3, \ N_2$$
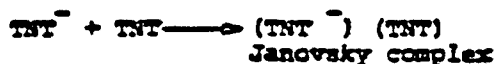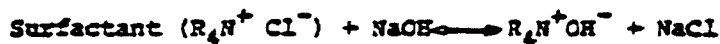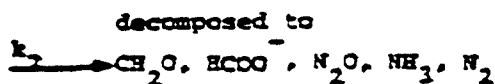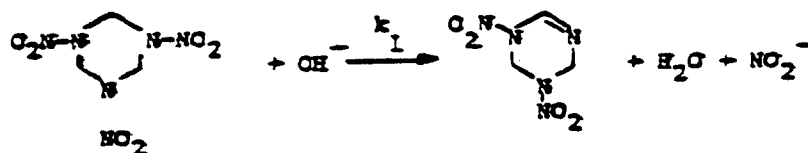
NITROCELLULOSE: HYDROLYSIS
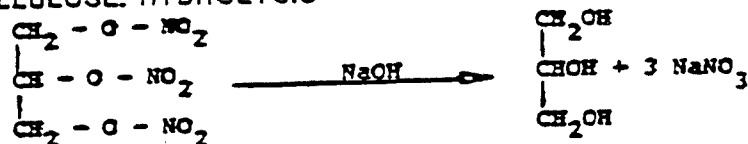
NITROGUANIDINE: HYDROLYSIS

$$HN:C(NH_2) \ NHNO_2 \longrightarrow HC:C(NH_2)N=N\cdot OH$$
$$O$$

$$+ \ NaOH \longrightarrow HN:C(NH_2)N=N\cdot ONa + H_2O$$

$$HN:C(NH_2)N=N\cdot ONa + NaOH \longrightarrow HN:C(ONa)N=N\cdot ONa + NH_3$$
$$O$$

$$HN:C(ONa)N=N\cdot ONa \longrightarrow HN:C(ONa)_2 + N=N=O$$

$$HN:C(ONa)_2 + H_2O \longrightarrow NH_3 + Na_2CO_3$$

46
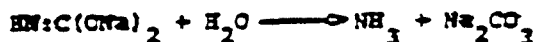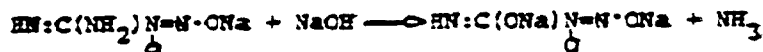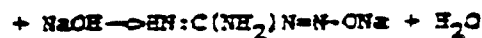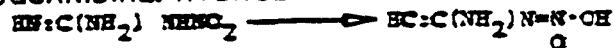
Prior Experience

Laboratory and pilot studies performed on pink water (TNT and RDX) have indicated that the complexing-hydrolysis process may be technically feasible and economically attractive (Freeman and Colitti, 1982). The reaction products and byproducts identified were the precipitated TNT-surfactant complex, RDX hydrolysis products, and alkali. Further identification of reaction byproducts was recommended, after which the suitability of a direct wastewater discharge or the need for further treatment can be determined. Reaction parameters of 25°C and a pH of 11 were used. The quaternary amine surfactant, Duoquad T-50, was found to be most effective at a mole ratio of about 0.4:1 (surfactant: TNT). Further optimization of the process was hampered by the lack of appropriate analytical procedures for TNT and RDX.

Studies performed by Okamato (1973) have demonstrated the increased rate of hydrolysis for RDX, HMX and nitroglycerin in the presence of the surfactant. The rates of hydrolysis and TNT precipitation were greatly increased by increasing the reaction temperature.

Soil leaching and mutagenicity studies of the TNT-surfactant complex were performed at the Natick Research and Development Laboratories (Kaplan and Kaplan, 1982). Ames mutagenicity testing indicated that a significant hazard is associated with the TNT-surfactant complex. The mutation rates caused by the complex were greater than those caused by TNT or the surfactant alone. Soil leaching studies were conducted by passing surfactant solutions through columns filled with TNT-contaminated soils. These studies indicated that a much higher molar ratio of surfactant to TNT (approximately 75-fold) is required for complexing TNT-laden soil as compared to TNT wastewater. The excess surfactant and sodium hydroxide were also found to cause leachate problems. The long term stability of the complex in a soil environment was found to be questionable. Moreover, the treatment itself was found to be ineffective in complexing the TNT reduction metabolites, 2-amino, 4,6-dinitrotoluene and 4-amino-2, 6-dinitrotoluene. For these reasons the use of the complexing-hydrolysis process for solid phase insitu treatment of explosive laden sediments is not recommended.

An additional study investigating the fixation of explosives in lagoon sediment by this process showed that the percolation of surfactant solution through soil resulted in the formation of a TNT-surfactant complex at the surface. This complex blocked further penetration of the soil thereby encapsulating the unreacted explosives. Core sampling revealed high concentrations of explosive beneath the surface (Freeman, 1982).

An ongoing feasibility study has indicated that surfactants are effective in removing tetryl from aqueous solution (Freeman, 1982).

Applicability to Lagoon Sediment

The feasibility of the complexing-hydrolysis process for treatment of lagoon sediments is questionable. Although the process has demonstrated potential for the treatment of pink water and the majority of explosives present in lagoon sediments (no data yet exists for nitrocellulose), it is unlikely that the approach will be workable with explosives in the solid phase. Communications with personnel familiar with this process indicate that laboratory testing is necessary to determine the feasibility of complexing-hydrolyzing a slurry of lagoon sediment.

Cost Factors

The major equipment costs of this conversion process are dependent upon the choice of having the reaction occur in the lagoon or as a sidestream in an adjacent vessel. The major chemical cost will be for the surfactant. Additional chemical cost will be incurred for sodium hydroxide and for the acid used in final neutralization.

Environmental Impact

The previously mentioned Natick studies have shown that the mutagenic property of the TNT-surfactant complex is greater than that of TNT (Kaplan and Kaplan, 1982). Numerous environmental problems are associated with solid phase insitu contacting; however, as this alternative is not viewed as workable, these problems will not be discussed.

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Only a few of the reaction products and byproducts from pink water treatment by this process have been identified. If this process were viable for slurry contacting, an investigation would be necessary to identify all products, determine their toxicity and establish the additional treatment necessary prior to discharge of the liquid stream or disposal of residual solids.

Alkaline Digestion of Nitrocellulose

Nitrocellulose is much less stable than most of the noninitiating military explosives. It undergoes decomposition slowly at ambient temperatures but the decomposition rate increases 3.7 times with each $10^{\circ}C$ temperature rise. The presence of moisture, acid and alkali increase the rate of nitrocellulose decomposition. Of these factors, alkali is the most effective in increasing the rate of decomposition (Army Technical Manual, 1967).

Nitrocellulose can be decomposed by a variety of alkaline digestion methods. Sodium hydroxide, barium hydroxide, sodium carbonate, and ammonium hydroxide can be used for the digestion. Of the above chemicals, sodium hydroxide has been found to produce a complete digestion at shorter contact times, lower digestion temperatures and lower concentrations for a given quantity of nitrocellulose (Wendt and Kaplan, 1976). Digestion with sodium hydroxide results in a complete degradation of the cellulose polymer. The main reaction products are various organic acids and sodium nitrate and nitrite.

Digestion with ammonium hydroxide also results in complete degradation of the cellulose polymer. This digestion is reported to yield end products with a commercial fertilizer value (Bissett and Levasseur, 1976). Although the use of ammonium hydroxide requires greater contact time, higher temperature and a higher alkali concentration, it may be preferable to sodium hydroxide because of the end products. The efficiency of either type of alkaline digestion is a function of contact time, digestion temperature, alkali concentration and nitrocellulose particle size.

Theory

Nitrocellulose is prepared by the nitration of cellulose, a polymer composed of a chain of anhydroglucose units ($C_6H_{10}O_5$). Depending on the degree of nitration a maximum of three nitro groups can be added to each anhydroglucose unit. Explosive grade nitrocellulose contains 2.6 moles of nitrogen per anhydroglucose unit.

The digestion of nitrocellulose with a strong alkali such as sodium hydroxide is reported to yield various hydroxy and polycarboxylic acids and sodium nitrate and nitrite. The use of ammonium hydroxide, a weaker alkali, reportly results in the formation of ammonium nitrate and nitrite from the nitrate ester groups. Ammonium salts of the carboxylic acids produced by the digestion are also expected (Bissett and Levasseur, 1976). The products and byproducts of alkaline digestion vary with the digestion conditions, alkali used and the presence of other compounds. Nitric oxides, ammonia and carbon dioxide gases can be evolved.

Prior Experience

There are many references in the literature regarding the digestion of nitrocellulose by alkali. A review of available literature indicated the formation of a wide variety of organic and inorganic compounds as the products of alkaline digestion. These compounds included inorganic nitrates and nitrites, ammonia, cyanide, carbon dioxide, nitrogen oxides, carbon monoxide, malic, oxalic, glycolic, trioxyglutaric, formic, dioxybutyric, malonic, tartronic and unidentified complex acids, sugars, and modified celluloses and their nitrates (Wendt and Kaplan, 1976; Kenyon and Gray, 1936).

The effects of alkali concentration, ratio of alkali to nitrocellulose, time, temperature and the degree of cellulose nitration on the digestion of nitrocellulose with sodium hydroxide were studied by Kenyon and Gray (1936). They determined that the time required to decompose a given weight of nitrocellulose decreases with increasing temperature and alkali concentration but is independent of the alkali-nitrocellulose ratio at

constant temperature. A given weight of nitrocellulose (2.5 percent) was found to decompose completely within 24 hours in a five percent sodium hydroxide solution at $30^{\circ}C$. When the same reaction was repeated at a temperature of $60^{\circ}C$, complete decomposition occurred within 50 minutes.

The digestion of five percent nitrocellulose in 1.5 to 3.0 percent solutions of sodium hydroxide, at contact times of 30 - 60 minutes and digestion temperatures of 95 to $98^{\circ}C$ has also been reported (Wendt and Kaplan, 1976). Experiments performed at Natick suggest that the sodium hydroxide digestion of nitrocellulose is an all-or-nothing decomposition of entire nitrocellulose units, rather than a stepwise denitration followed by degradation of the cellulose polymer. The use of sodium hydroxide digestion as the initial step of an integrated chemical-biological treatment process was investigated during this study.

Nitrocellulose digestion studies were reported using ammonium hydroxide at a temperature of $73^{\circ}C$ (Dogliotti, et al, 1974). Nitrocellulose concentrations varied from 5 to 15-percent as did the ammonium hydroxide concentrations, and the contact time varied from 4 to 24 hours. The study results indicated that the reaction could be optimized for contact time or economics; a 10-percent nitrocellulose solution was degraded completely with a 10-percent ammonium hydroxide solution at $73^{\circ}C$ for 10 hours. Analysis of the reaction products indicated that breakdown of the cellulose polymer took place.

Studies performed by Bissett and Levasseur indicated that ammonium nitrate was formed by the digestion of nitrocellulose with ammonium hydroxide (1976). All experiments were performed using a 5-percent nitrocellulose solution. The reaction time, temperature and ammonium hydroxide concentration were varied. Experiments were performed in both closed and open systems; a 5-percent solution of nitrocellulose was completely decomposed in three hours in a closed reactor by a 5-percent ammonium hydroxide solution at $90^{\circ}C$. The use of a closed reactor resulted in substantial savings in ammonium hydroxide and/or a reduction in reaction time. Experiments performed at room temperature indicated that high concentrations (up to 29 percent) of alkali and long reaction times (up to

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120 hours) were required for digestion (Bissett and Levasseur, 1976).
Reaction at high temperatures, although more efficient, resulted in the
formation of gaseous products (NO_x and CO_2), probably from the breakdown of
ammonium nitrate and nitrite.

A feasibility study of the landfilling of nitrocellulose lime sludge
was performed by Envirex (Huibregtse, et al, 1979). Cyanide was identified
as a substantial degradation product. Although most of the cyanide was in
a complex organic form and remained entrained in the sludge, some free
cyanide was observed to have leached from the sludge.

Applicability to Lagoon Sediments

Based upon prior experience alkaline digestion is a viable alternative
for the treatment of nitrocellulose contaminated sediments. Although this
alternative will also result in the hydrolysis of RDX, HMX and
nitroglycerin, the reaction with TNT may result in the formation of
dangerously sensitive compounds (or an explosion), depending upon the
alkali and reaction conditions used (Army Technial Manual, 1967; Urbanski,
1964). For this reason the alternative is not recommended at this time for
sediments containing TNT.

Depending on the characteristics of the lagoon, it may be possible to
digest a slurry containing nitrocellulose in the lagoon. The major
advantage of this approach is that long reaction times would be feasible.
The longer reaction times can alleviate the need to add heat to the
digestion. The rate of release of gaseous products is minimized at lower
reaction temperatures. In addition, this may increase the yield of
ammonium nitrate which is high in fertilizer value.

The use of a closed reactor is recommended if the digestion is to be
done on a sidestream in an adjacent vessel. This would allow the efficient
use and reuse of heat and lessen the chemical requirements. The optimum
amount of heat to add is a trade-off between the considerations of reaction
time, gaseous emissions, chemical requirements and desired end-products.

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The choice of alkali (sodium hydroxide or ammonium hydroxide) is dependent on the chemical costs, equipment costs, environmental impacts and required end products. According to Bissett and Levasseur (1976), digested nitrocellulose is amenable to biological treatment; however, the presence of toxic substances in the sediment may limit this approach. For example, one characterization of a lagoon sediment containing nitrocellulose indicates that diethyl and dibutyl phthalates are present in high concentrations (> 1000 mg/l) (ESE, 1982). These compounds are used to gelatinize nitrocellulose but are also listed as priority pollutants. The effect of alkaline digestion on these compounds has to be determined.

Cost Factors

As in all alternatives the major equipment costs of alkaline digestion will vary with the selected initial and secondary material handling alternatives. Chemical costs will vary with the concentration of nitrocellulose, the competing chemical demand present and the potential need for acid for final neutralization. The optimum dosage, operating conditions, utility requirements (heat) and post-treatment needs will be site-specific.

Environmental Impact

The environmental impact of alkaline digestion will be dependent upon the choice of alkali, reaction conditions, concentration of nitrocellulose and equipment used. Gaseous products such as nitric oxides, carbon dioxide and ammonia are expected during high temperature digestion. Digestion products and byproducts must be identified and evaluated for toxicity (cyanide reported in the literature). The toxicity of compounds such as phthalates present in the initial sediment must also be determined. It may also be necessary to enclose the reactor and to treat the gaseous byproducts.

Gamma Irradiation

Gamma rays are electromagnetic energy waves emitted during radioactive decay. Gamma rays are very penetrating; a layer of water 25 inches deep is

required to stop 90 percent of the rays from a Cobalt 60 source. For this reason exposure to gamma rays emitted from selected isotopes (gamma irradiation) has been used for disinfection of sewage sludge. Gamma rays are continuously emitted at a relatively constant rate; therefore the applied energy can only be varied by exposure time. Two isotopes, Cesium 137 (Cs-137) and Cobalt 60 (Co-60), have been used as gamma ray sources.

The treatment of explosive-contaminated lagoon sediments by gamma irradiation was investigated by the ARC (Wentsel, et al, 1981). They proposed that explosive degradation by gamma irradiation, electron beam processing and ultra-violet ozonolysis all proceed by a similar degradation pathway. The proposed mechanism for decomposition by gamma irradiation is hydroxyl ion formation. This formation is enhanced in the liquid state (Disalvo, 1983).

Prior Experience

Two types of gamma irradiation processes have been developed for sludge disinfection, dry and liquid (EPA, 1979). A research facility to treat dry sludge was constructed by Sandia Laboratories in New Mexico. This facility was designed to treat eight tons per day of dried sludge using a one-million curie Cs-137 source. a conveyor system is used to transfer and expose the sludge to the gamma radiation source. The City of Albuquerque, New Mexico, has approved the design of the first municipally-owned and operated sludge irradiation facility in this country. The proposed plant will be designed to process 10,740 dry tons of sludge per year (ENR, 1963; C&E News, '983).

A liquid sludge treatment facility was constructed and operated on a demonstration basis in West Germany in 1973. Although this facility was designed to treat 40,000 gallons per day, the initial Co-60 charge was only sufficient to treat 8,000 gallons per day. A diagram of the liquid sludge treatment facility is shown in Figure 11. Sludge is pumped into the source cavity and recirculated in the batch mode for the desired exposure time.

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FIGURE 11. LIQUID SLUDGE GAMMA IRRADIATION FACILITY AT GUSELBULLACH, WEST GERMANY (EPA, 1979)
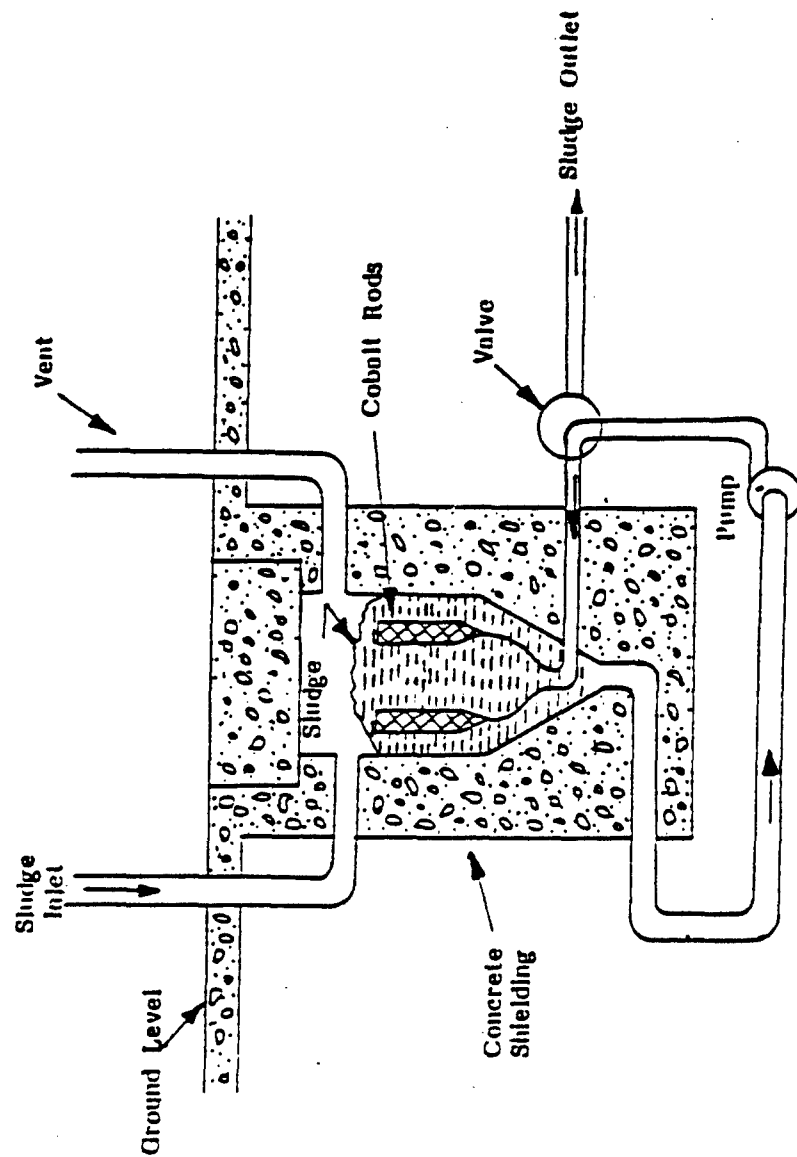
The efficiency of gamma irradiation for treatment of polychlorinated biphenyls was found to be solvent-dependent. A maximum of 20 percent PCB destruction was obtained using a 15 percent ethanol/85 percent water solvent, while total destruction was obtained in a alkaline/2-propanol solvent (Wentsel, et al, 1981). Exposure of pink water to gamma radiation from a Co-60 source was highly successful. The TNT content of the water was reduced from 89 mg/l to 2 mg/l (Wentsel, et al, 1981).

The effectiveness of thermoradiation processes which utilize the synergistic effects of heat and gamma irradiation was investigated by Sandia Laboratories. A 70 percent reduction in gamma dosage was achievable when sludge was disinfected at 55°C (Ahlstrom, et al, 1977).

Applicability to Lagoon Sediments

The liquid sludge gamma irradiation process is applicable to the desensitization of explosive contaminated lagoon sediments. Unlike ultraviolet radiation, the penetrating power of gamma radiation should not be hindered by the presence of sediments and high-explosive crystals. However, the sediments would have to be resuspended and removed from the lagoon at the maximum feasible solids concentration and pumped into the source cavity for recirculation until desensitization is achieved (batch operation). The recirculation would also ensure that the slurry remains mixed. If justified by laboratory studies, air or oxidants (e.g., ozone; peroxides) could also be added during recirculation.

As recommended by ARC (Wentsel, et al, 1981), the gamma irradiation unit should be buried or placed in a bunker to provide shielding. Adequate safety and handling procedures and equipment must also be included. The cost and practicality of transportation of the unit and source must be determined. Transportation costs can be minimized by selecting sites which contain several lagoons requiring treatment.

As in all alternatives, laboratory and pilot testing would be necessary to determine the optimum conditions for gamma irradiation. Investigations should also be conducted to determine alternate irradiation methods.

Cost Factors

The costs of gamma irradiation by means of a liquid slurry treatment
system were developed for the EPA by Battelle Pacific Northwest
Laboratories (Ahlstrom, et al, 1977). Cost elements for the facility
included:

o insulated concrete building

o equalization sludge storage tank

o emergency water dump (source shielding)

o irradiating capsules (source)

o steel lined source handling pool

o deionizer

o data acquisition and control system

o oxygen injection facility

o pumps, piping, and flow meters

o radiation alarms

o fire suppression system

Operating costs were also estimated by Battelle.

The Battelle estimates were developed for a permanent facility. For
comparison purposes in this study these estimates were adjusted to 1982
dollars but no estimates were developed for dismantling and transportation
or for permitting.

Environmental Impact

The environmental impact of gamma irradiation is dependent on the
treatment conditions used and on the lagoon sediment itself. For long
contact times, gaseous products such as NO_x, CO_2, CO, and SO_x are
anticipated (Wentsel, et al, 1981). The characteristics of the liquid
effluent are unknown at this time but should be low in organics if
sufficient contact time is provided. Laboratory and pilot scale testing
should be performed to determine the final products of gamma irradiation.

BIOLOGICAL CONVERSION PROCESSES

Biological waste treatment encompasses the anaerobic, anoxic and/or aerobic decomposition of organic matter using either suspended or attached growth microbial populations in a supportive environment. The factors combining to make an environment supportive for biological decomposition include pH, temperature, nutrient and micronutrient availability and dissolved oxygen supply or lack thereof. There are many configurations possible for biological waste treatment systems including the suspended culture and composting systems that have been studied or applied to the decomposition of TNT, RDX and HMX.

Research conducted in recent years has enhanced the information available for specifying a biological waste treatment system for explosive compounds. For example, it is now evident that TNT undergoes both aerobic and anaerobic breakdown, RDX and HMX decompose only by anaerobic pathways and nitrocellulose is not amenable to biological decomposition by either pathway. As a result of this experience, aerobic biological treatment is not universally applicable for treatment of explosives. It is also evident that TNT, RDX and HMX decompose biologically only at concentrations considerably less than the solubility limits of the compounds, that the primary mechanisms of decomposition are via successive reductions of the nitro groups and that the decompostion of these explosives is supported synergistically by the presence of other more decomposible forms of organic carbon in the biological reactors. It is also recognized that TNT, RDX and HMX have toxic effects on many aquatic test organisms and that the biological decomposition products are often more toxic and mobile than the explosives themselves. Much of the knowledge gained has been at the mechanistic level, e.g., definition of biotransformation pathways, and it is from this point that engineering development must commence.

Theory

The biological conversion of TNT takes place both aerobically and anaerobically as the successive reduction of the nitro groups; in either

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case without the cleavage of the ring structure (McCormick, et al, 1976;
McCormick, 1982). Anaerobically, the successive reduction is to
hydroxylamino compounds with no evidence that the amino compounds are
combined with carbonyl compounds to form insoluble complexes. Similarly,
it is believed that the compounds formed in the aerobic treatment of TNT
dimerize to form azoxy compounds that are bound into floc. In either case
a carbon source and an effective reducing agent are required, as well as a
neutral pH and the complexing of heavy metals if present. In addition,
adequate mixing is required to promote the solubilization of TNT and
contact between the soluble TNT and the microbial population. The work of
Nay et al (1974) was the only reference reviewed in which rate constants
characterizing the aerobic biotransformation of TNT were found.

The anaerobic biological conversion of RDX and HMX takes place via
denitrification pathways resulting in the production of hydrazines (a
chemical reductant), formaldehyde, methanol and nitrogen (McCormick, 1982;
McCormick, et al, 1981). Formaldehyde and methanol are further decomposed
to methane and carbon dioxide. Nothing could be found in the literature to
document the reaction rates for RDX and HMX biotransformation. However,
McCormick's work at the laboratory scale indicated that these compounds
convert fully within two weeks (1981).

Work by Wendt and Kaplan (1976) has shown that nitrocellulose cannot be
treated biologically without an initial chemical treatment to hydrolyze the
nitro groups. Inasmuch as the chemical treatment itself is sufficient to
accomplish the desensitization of nitrocellulose, the further biological
treatment of the residues is not warranted solely for desensitization
purposes.

A major constraint to predicting the efficacy of biological waste
treatment for lagoon soils and sediments is the absence of information on
the kinetics of solubilization and biotransformation. The literature is
replete with information on the biotransformation of explosives in solution
phase. The explosives of concern are compounds of limited solubilities at
ambient temperatures (in the order of 100 mg/l), such that 99 percent of
the explosives content would still be in solid form at a bulk explosives

concentration of just one percent. If, under the conditions encountered in a desensitization operation, the solubilization rate is less than the biotransformation rate, an entirely new set of limitations would control the operation. For purposes of this analysis, it is assumed that the biological transformation of TNT, RDX and HMX can take place only in the solution phase.

Configuration

Biological waste treatment can be provided aerobically or anaerobically using suspended growth or attached culture systems in a liquid medium, or attached culture systems in a solid medium. Included in this classification system are the following commonly used configurations:

o   Liquid-medium, suspended growth systems: aerated lagoons; facultative ponds; anaerobic ponds; activated sludge systems; anaerobic digesters; aerobic digesters

o   Liquid-medium, attached culture systems: fixed-film, packed bed and fluidized bed reactors (anaerobic or aerobic)

o   Solid-medium, attached culture systems: composting

The various configurations have evolved as engineers have sought different methods to attain the longer solids retention times and good mixing essential for production of high quality effluents simultaneously with attaining lower liquid or hydraulic retention times.

Composting is the variation of biological waste treatment in which a solid matrix is used to support the decomposition. The solid matrix consisting of the waste material, bulking agents to provide the carbon and nutrient sources, pH adjustment, proper water content and porosity serves to support a symbiotic anaerobic-aerobic environment. The matrix formed by a mixing operation consists of an inner (anaerobic) environment and an outer (aerobic) layer. The bounds of the aerobic layer are defined by the oxygen transfer from the pores of the matrix into its mass.

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In order for composting to take place at thermophilic temperatures (50 to 60°C), the mass ratio of water to organic matter cannot exceed a critical limit without either limiting oxygen transport (too little air) or excessive cooling of the pile (too much air). Thus composting has as its unique features the bulking requirement, with attendant dilution of the bulk density of a waste component; a limiting water content (delimiting the quantity of a substance that can be in solution); a symbiotic anaerobic/aerobic environment and (if properly conducted) a thermophilic temperature range. In addition, the composting process requires several materials handling steps not required in the liquid medium methods and significant volumes of bulking materials (e.g., 3 to 4 cu yd per wet ton at 20% solids).

From a process design viewpoint, the biological waste treatment processes can be conducted on a batch, fill and draw or continuous flow basis. Batch processing, such as the aeration of a lagoon or of a static compost pile for selected times periods, can proceed until the substrate is depleted or toxic products accumulate. Fill and draw or continuous flow processing requires the intermittent or continuous removal of residual solids to control the solids inventory such as accomplished by clarification in the activated sludge system or by retrieval units in enclosed mechanical composting sytems.

Applicability

There is little question that biological waste treatment processes are applicable for the desensitization of lagoon sediments. The principal deterrent to the selection of a preferred configuration is the absence of kinetic (rate) constants for the various configurations. Without the capability of predicting the performance of a given configuration, comparative cost and performance information cannot be developed.

A review of the literature was made to identify the information base available for comparing TNT and RDX bioconversion rates and for comparing liquid and solid media biological systems. An analysis of the available

information on the biological conversion of TNT and RDX is presented in Volume Two. The findings of this analysis, providing useful insight to the applicability question, are as follows:

(1) Composting systems operating in the thermophilic temperature range ($50-60^\circ$C) attained bioconversion rates on a bulk-volume basis that were six to eight-fold less than on a water-volume basis. Thus, only one-sixth to one-eighth of the bulk volume of a composting system is used when solution-phase biological conversion is required.

(2) The water-volume basis bioconversion rate for TNT (0.13 lb/cu ft-day) in the thermophilic temperature range is at least one order of magnitude greater than estimated from the work of Nay et al (1974) at ambient (10°C) temperatures. A difference of this magnitude suggests that major reductions in retention times may be achievable when liquid phase systems are operated at thermophilic temperatures.

(3) The bioconversion rate for RDX at thermophilic temperatures was approximately one-sixth to one-eighth that for TNT on a water-volume basis.

The lack of definitive and complete information of this nature essentially precludes the rational engineering analysis of alternative bioconversion systems for desensitization. For purposes of this investigation, it was assumed that long detention times, substantial dilution of the solubilized explosive (relative to its saturation concentration) and high supplemental reductant (carbon source) concentrations are required. It was also viewed as premature to render a judgment about the relative merits of any configuration until biological rate studies such as recommended in Chapter 7 are conducted. Upon completion of these studies, a preliminary engineering and economic analysis of the various preferred configurations will be possible.

For comparative evaluation purposes, it was assumed that a liquid-medium system could be used for desensitization, that TNT could be desensitized aerobically or anaerobically, that RDX and HMX could be desensitized anaerobically and that nitrocellulose cannot be desensitized biologically. It was further assumed that the lagoon sediment would be excavated hydraulically, resuspended and desensitized either insitu or in an adjacent closed thermophilic reactor. Appropriate water control measures would be used as necessary; the sediment would be kept mixed by either an aeration system or by recirculation. In either case, it was assumed that the slurry would not be desensitized until the explosives were solubilized and biotransformed. If necessary, air scrubbers would be provided for odor control and toxic metals would be sequestered by the addition of soluble sodium sulfide.

Cost Factors

The major equipment cost for biological treatment is for the lagoon suspension and aeration or recirculation system. Additional costs would be incurred for supplemental sludge pumping and chemical addition (if required). If anaerobic treatment is selected, it was assumed that a lagoon cover would be required. It would be necessary to construct an adjacent reactor vessel if the characteristics of the lagoon do not permit insitu contacting.

Environmental Impact

The major environmental impact of both biological treatment processes results from the expected toxicity of the products and byproducts of desensitization. The lagoon would have to be isolated from groundwater to prevent contamination. It is expected that hydrogen sulfide emitted during anaerobic treatment would require scrubbing before release of the gas stream. A lagoon cover is impractical for the envisioned system. Developmental studies would be needed to determine both the products and byproducts of desensitization and their toxicity.

THERMAL CONVERSION PROCESSES

Three thermal conversion processes were reviewed for their adaptability to desensitization of lagoon sediments: thermal decomposition incineration and wet-air oxidation. Of these, the latter two were ultimately selected for evaluation.

Thermal Decomposition

Thermal decomposition of explosives has been proposed as a building decontamination method by Battelle Laboratories (Mezey, et al, 1982). Explosives undergo thermal decomposition at temperatures below those at which a spontaneous explosion can occur and the decomposition products are primarily gaseous. Decomposition temperatures and contact time requirements vary from 100 to 350°C and from one second to one year. A temperature of 250°C is required for 99 percent TNT decomposition within a one-week period.

The adaptability of this process for the desensitization of lagoon sediment is limited by the reactivity of the sediment. According to tests conducted by the U.S. Army Research and Development Command (Kirshenbaum, 1981), the sensitivity of explosives is increased by the addition of humus (soil). Sediment mixtures containing at least 10 percent by weight of explosives are thermally active and could burn when heated to 175 to 200°C. Although this hazard is eliminated at an explosives concentration of five percent, lagoon characterization data indicate the likelihood that pockets of high explosive concentrations would be encountered. An additional problem with this approach is that, if drying were to occur, the sensitivity of the explosive mixture would be increased. On the basis of these considerations it was decided to eliminate thermal decomposition from further consideration.

Incineration

Incineration is currently being developed as an interim treatment for explosive-laden lagoon sediments by another USATHAMA contractor. USATHAMA

has indicated that incineration should be considered as a baseline against which the desensitization alternatives developed in this study are evaluated. For these reasons, discussion on incineration has not been included in this study. However, costs and technical information developed by ARC (Wentsel, et al, 1981) were updated and used for the evaluation and ranking of alternatives.

Wet-Air Oxidation

The wet-air oxidation process is both a desensitization technology and a post-desensitization treatment approach. This process was evaluated as an overall treatment approach for explosive sediment by ARC (Wentsel, et al, 1981). Their evaluation was based upon several pilot studies in coordination with Zimpro, a systems vendor. The recommended system included post-treatment of the oxidized slurry and air pollution control equipment. For purposes of this study the technical and economic data from ARC have been used to develop wet-air oxidation treatment alternatives.

Theory

Wet-air oxidation is a process in which organic substances are oxidized chemically in an aqueous phase at elevated temperature and pressure in a specially designed reactor. The principal components of this process, shown in Figure 12, are a high pressure pump, heat exchanger, reactor and air compressor. Organic material is preheated in the heat exchanger and then pumped into the reactor with compressed air. Oxidation occurs in the reactor (catalysts may be used) at temperatures varying from 177 to 320°C, and pressures of 1,000 to 1,800 pounds per square inch absolute (psia). The oxidized slurry is cooled by the heat exchanger and then gases are stripped and the ash separated. The gases are reduced to atmospheric pressure and treated to eliminate odors before release.

Prior Experience

The wet-air oxidation process has been used to condition both municipal and industrial sludges. The process has also been used to degrade

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FIGURE 12. BASIC WET-AIR OXIDATION FLOW SCHEME (WENTSEL, et al., 1981)
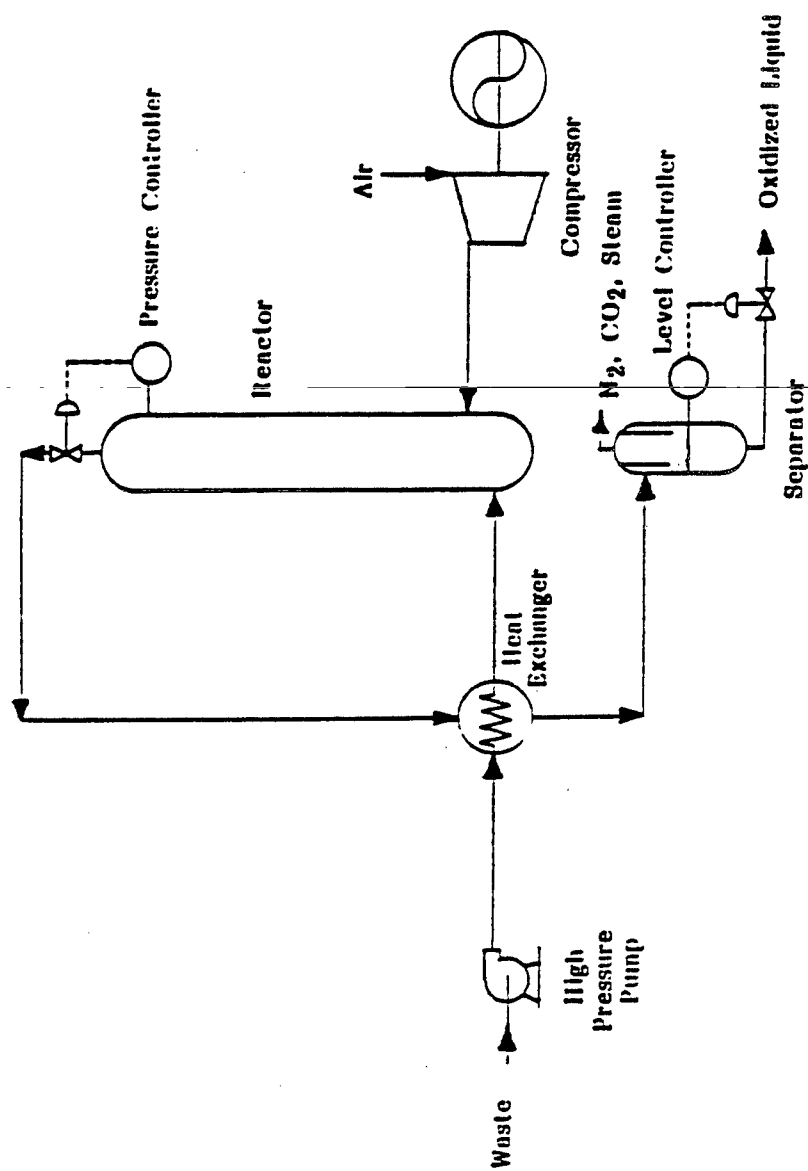
hazardous chemicals and herbicides. Although wet-air oxidation was generally successful in degrading toxic compounds, significant amounts of chlorinated organics were not degraded (Wentsel, et al, 1981).

Zimpro performed pilot studies on waste propellants (primarily nitro-cellulose and nitroglycerin). The solid propellants were slurried in a water-acid mixture and oxidized at $204°C$ and 815 psia for a three-hour period. Zimpro reported a minimum propellant destruction of 97.6 percent. ARC found the analytical results and mass balance procedure used by Zimpro questionable (Wentsel, et al, 1981). Although it was also reported that other pilot studies on propellants and TNT red water had resulted in removal rates of 96-99 percent, experimental details were not available.

Applicability to Lagoon Sediment

The wet-air oxidation system considered herein is the same as that recommended by Zimpro and described in the ARC report. Depending on the site, the sediment would be either slurried in the lagoon to a solids concentration of say five percent, or removed from the lagoon to a holding tank and slurried in a mixing tank. The slurry would then be processed by the wet-air oxidation unit. If required by the overall approach, the reactor effluent would be neutralized by addition of sodium hydroxide. Unlike the Zimpro and ARC processes, biological treatment of the reactor effluent is not anticipated for desensitization purposes.

Cost Factors

The cost of the basic wet-air oxidation system was updated from the ARC report. In order to be consistent with the incineration alternatives, the cost of an air pollution control system was included. In an installation, the cost of the initial materials handling and necessary secondary materials handling equipment would be dependent upon the characteristics of a specific lagoon. The cost of neutralization of the reactor effluent would be included only if it is required by the overall approach.

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Environmental Impact

The effluent of the wet-air oxidation process is expected to be high in COD, solids and BOD. Carbon monoxide and nitrous oxides are anticipated reactor byproducts; toxic heavy metals may also be present. The inclusion of an air emissions control system should minimize the release of the gaseous products. The fate of other pollutants present in the sludge would have to be determined in laboratory/pilot studies.

UNDEVELOPED CONCEPTS

A number of concepts have been suggested for which theoretical and/or empirical documentation is limited or unavailable. The lack of information has prevented the degree of evaluation needed for rank ordering of these concepts, which are described and discussed below.

Lagoon Detonation

It has been proposed that the lagoons be detonated insitu by an initiating explosive. The effectiveness of this process would be dependent upon the explosive concentration and moisture content, and other sediment characteristics. If all explosives were not detonated completely, they would be scattered over a wide area, thereby expanding the area of contamination, with ultimate risk of surface and underground contamination of aquifers.

Safety is an additional consideration. Due to the lack of records and characterization data on the lagoons, the size of the explosion would be difficult to predict, and possible damage to base and private facilities from the explosion and blast concussion must be considered.

Open Burning

The open burning and/or detonation of waste explosives is permitted under the Resource Conservation and Recovery Act (Federal Register, 1980). Waste explosives by definition "include waste which has the potential to

detonate and bulk military propellants which cannot be disposed of through
other modes of treatment." However, waste explosives must be burned or
detonated "in a manner that does not threaten human health or the
environment."

The spreading and ignition of explosive sediments with waste
oils/solvents has been proposed. It is unclear if explosive sediments are
included in this regulation since processes can be identified which
incorporate a greater degree of air emission control during destruction.
In addition the amount of fuel equivalent needed for burning would depend
upon the characteristics of the sediment and may be quite high for
sediments with a low explosive but high water content.

Surfactant-Oil Complexing

The mixing of explosive sediments with "ivory snow" and diesel fuel was
also identified as a desensitization method; however, documentation on this
process could not be found. It was suggested that the surfactant-oil
complex forms a stable flammable gel which can either be used as a
supplemental fuel or easily incinerated. Because the emissions from either
type of combustion can be controlled, it should be possible to conduct the
test burns requisite for regulatory agency acceptance. This process may be
most applicable to sediments containing a high concentration of explosives
which otherwise would present handling problems.

Oxidation by Fenton's Reagent

Fenton's reagent, a solution of aqueous ferrous sulfate and hydrogen
peroxide, is a highly reactive oxidizing system. Although literature was
not located concerning its use for oxidizing explosives, references were
found for the oxidaton of other nitroaromatics by this system. It is
envisioned that Fenton's reagent may be applied in the same manner as other
desensitizing chemicals or used in conjunction with gamma irradiation to
lower dosage requirements.

CHAPTER 4

ALTERNATIVES FOR DESENSITIZATION

The alternatives presented in this chapter consist of each of the conversion processes combined with the appropriate initial materials handling, secondary materials handling and separation processes necessary to accomplish the desensitization. Desensitized material usually requires further treatment to be acceptable for final disposal. To this end additional unit processes are proposed with each alternative to provide a complete system.

It is appropriate that desensitization alternatives consider these processes because the added cost of post-desensitization treatment (PDT) may be offset by a savings elsewhere in the system. An example of this would be the recycling of a desensitized effluent to fully deplete a toxic chemical reactant prior to biological treatment. Another example would be the dewatering or hydraulic classification of lagoon sediment prior to incineration to reduce supplemental fuel requirements and possibly result in an overall system cost savings.

Logic diagrams can be used to define and identify the alternatives for desensitization, and are applied in this chapter to develop the alternatives around each conversion process. Additional alternatives are also defined when the PDT requirements are considered. The approach outlined in this chapter provides a framework adaptable to the eventual computer modeling of the desensitization alternatives.

DEVELOPMENT OF ALTERNATIVES

A series of seven simplified logic diagrams have been developed to identify and define the desensitization alternatives. Each diagram is used to illustrate the assignment of one digit of a 7-digit identification number unique to each alternative. The logic diagrams are used in a pre-defined sequence, and in conjunction with lagoon characterization data, to define all feasible combinations of conversion processes and contacting

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schemes for the given set of lagoon characteristics. An initial materials handling method is then selected and any necessary water control measures are identified for each combination. The equipment required to accomplish desensitization and PDT (if desired) is then defined. At the end of this sequence each feasible alternative can be identified by the 7-digit identification number. The feasible alternatives are then evaluated and rank-ordered by comparison (Chapter 6).

Each logic diagram refers to a specific process or operation, as follows:

o   Initial Process Selection

o   Process Enhancement

o   Feasible Contacting Methods

o   Initial Materials Handling

o   Water Control Measures

o   Basic Treatment Train

o   Post-Desensitization Treatment

The logic diagrams are explained briefly below. The numbering system used for all of the logic diagrams is shown in Table 2.

Initial Process Selection

The initial process selection diagram, shown in Figure 13 is used to identify those desensitization concepts or processes which are not applicable for a given set of lagoon characteristics. For example, aerobic biological treatment is not applicable if RDX is present in the lagoon. Each applicable process is then considered in turn by working through the other logic diagrams. The first digit of a 7-digit identification number corresponds to the process under consideration.

Process Enhancement

This diagram, shown in Figure 14, identifies methods for enhancing the conversion processes; not all methods are applicable to all processes. Two

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TABLE 2.   ALTERNATIVE NUMBERING SYSTEM

CONVERSION PROCESS -   First Digit (Figure 13)

      0   Alkaline Digestion by NaOH
      1   Alkaline Digestion by NH_4OH
      2   Complexing-Hydrolysis
      3   Chemical Reduction by Inorganic Reductants
      4   Chemical Reduction by Organic Reductants
      5   Gamma Irradiation
      6   Incineration
      7   Wet-Air Oxidation
      8   Anaerobic Biological
      9   Aerobic Biological

PROCESS ENHANCEMENT -   Second Digit (Figure 14)

     x0   None
      1   Heat (Cover needed)
      2   Solvents
      3   Co-solvents
      4   Surfactants
      5   Salts
      6   Radical Traps
      7   Supplemental Fuels (Waste oils/solvents)
      8   Hydraulic Classification
      9   More than one

FEASIBLE CONTACTING METHODS -   Third Digit (Figure 15)

    xx1   Solid Phase
    xx2   Insitu Lagoon
    xx3   Sidestream

INITIAL MATERIALS HANDLING -   Fourth Digit (Figure 16)

    xxx1   Injection Techniques
      2   Hydraulic Resuspension, Short Duration
      3   Hydraulic Resuspension, Extended Duration
      4   Hydraulic Resuspension, Short Duration with Chemical
         Addition
      5   Hydraulic Resuspension, Extended Duration with Chemical
         Addition
      6   Hydraulic Excavation, Minimal Dilution
      7   Hydraulic Excavation, Minimal Dilution, Chemicals Added
      8   Hydraulic Excavation, Dilution
      9   Hydraulic Excavation, Dilution, Chemicals Added

WATER CONTROL MEASURES -   Fifth Digit (Figure 17)

   xxx-x0   Construct Water Channel
      1   Add Water

TABLE 2.   ALTERNATIVE NUMBERING SYSTEM (Continued)

2   Use Well Points in/below Embankment
3   Use Well Points in Embankment
4   Use Well Points in Lagoon
5   Add Water Continuously or Infeasible
6   Line Perimeter
7   Dike Repair/Construction

BASIC EQUIPMENT TRAIN - Sixth Digit (Figure 18)

xxx-xx0   Open System
    xx1   Open System, Holding Required
    xx2   Open System, Chemical Feed
    xx3   Open System, Chemical Feed and Reactor
    xx4   Open System, Chemical Feed, Holding and Reactor
    xx5   Closed System, Cover Required
    xx6   Closed System, Holding Required
    xx7   Closed System, Chemical Feed
    xx8   Closed System, Chemical Feed and Reactor
    xx9   Closed System, Chemical Feed, Holding and Reactor

POST DESENSITIZATION TREATMENT - Seventh Digit (Figure 19)

xxx-xxx0   Direct Discharge (to WWPT, other trains)
    1   Neutralization
    2   Recovery/Concentration
    3   Solid/Liquid Separation
    4   Solid/Liquid Separation with Neutralization
    5   Solid/Liquid Separation with Recovery/Concentration

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FIGURE 13. INITIAL PROCESS SELECTION – FIRST DIGIT

FIGURE 14. PROCESS ENHANCEMENT – SECOND DIGIT

76
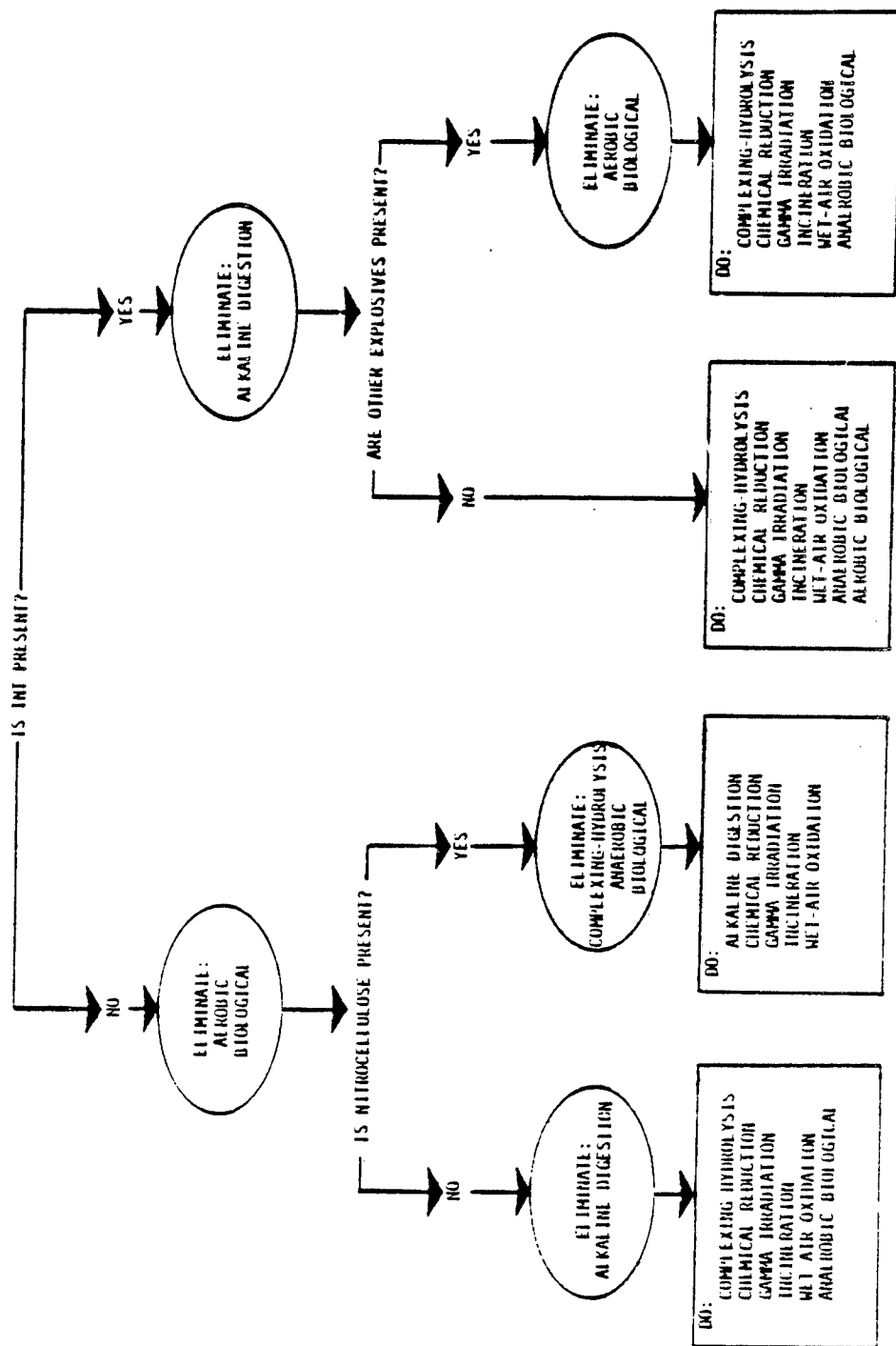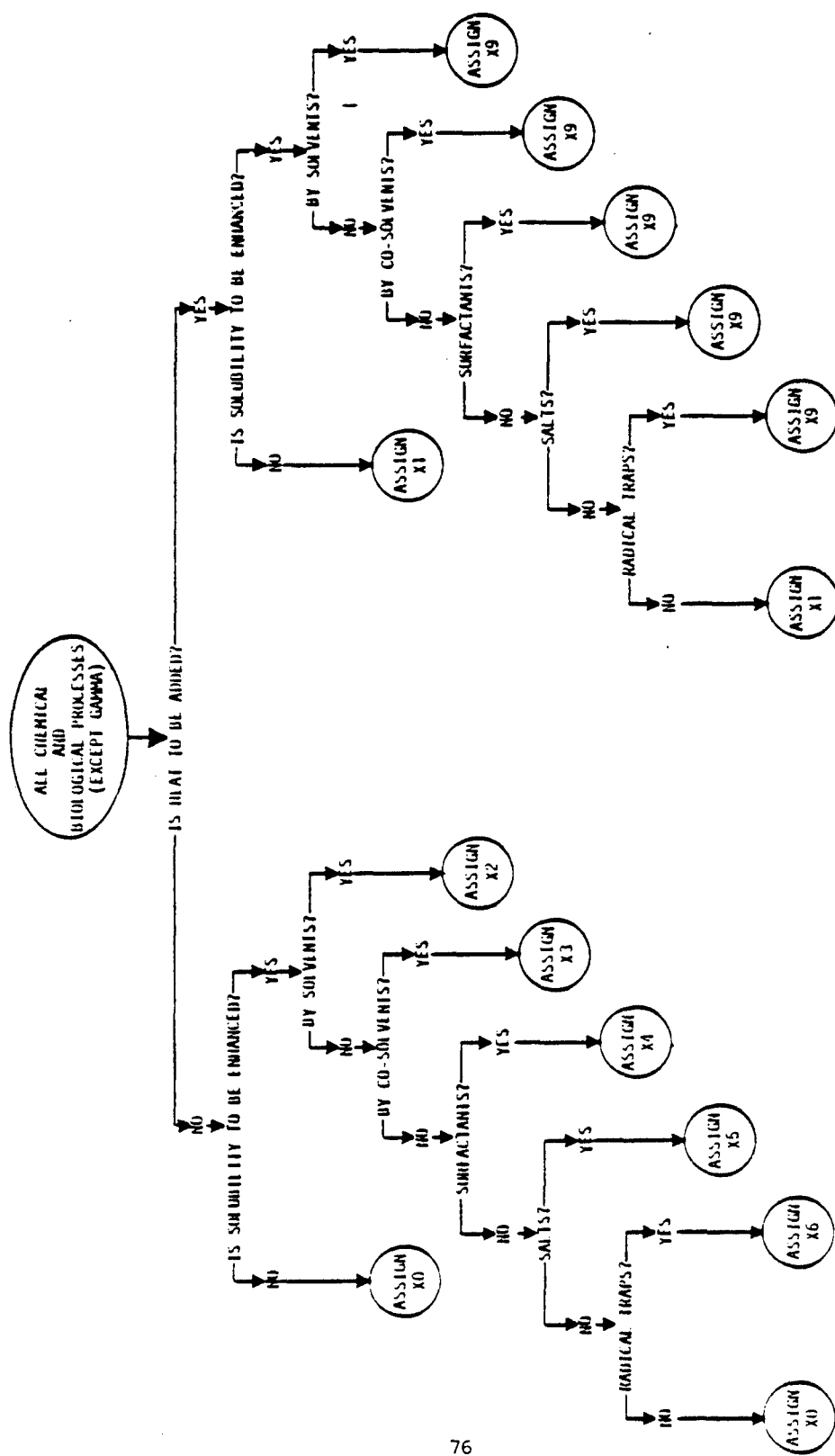
FIGURE 14. PROCESS ENHANCEMENT (Continued)
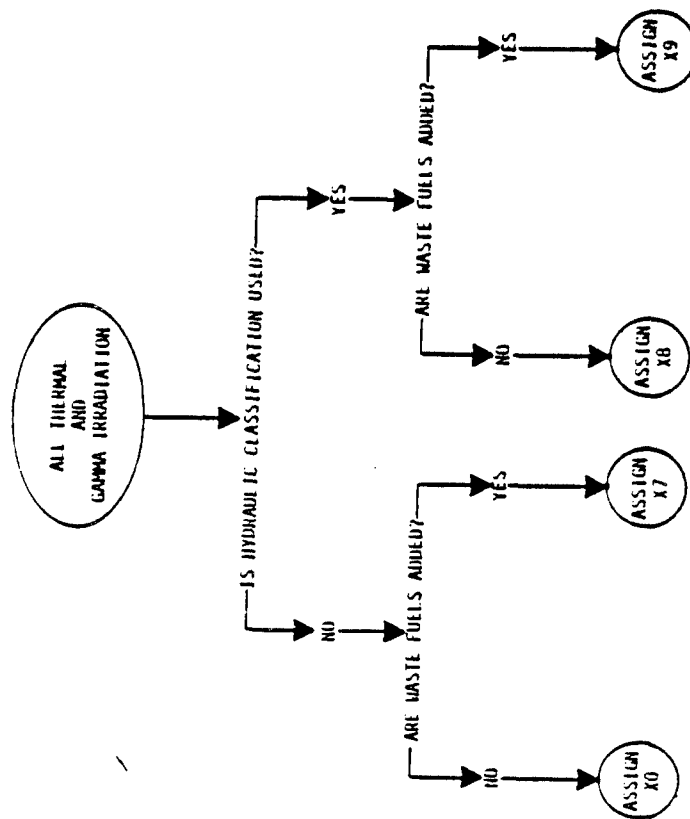
pathways are provided. The first, intended for all biological and chemical processes (excluding gamma irradiation), includes enhancement by means of heat addition or increasing the solubilities of the explosives. The second pathway, intended for all thermal processes and gamma irradiation, concerns the use of hydraulic classification and the addition of waste solvents/oils for process enchancement. The second digit of the 7-digit identification number is assigned at the bottom of the logic diagram.

Feasible Contacting Schemes

The logic diagram, shown in Figure 15 identifies which of the three available contacting schemes (solid phase; liquid/lagoon; liquid/-sidestream) are feasible for a given set of lagoon characteristics. The conversion processes that were identified previously as applicable are matched with the feasible contacting schemes. If more than one contacting method is feasible and available for the proposed conversion process, then all will be considered in turn. Table 3 lists the available contacting schemes for each conversion process. The third digit of the identification number is assigned to the selected contacting method.

Initial Materials Handling

The initial materials handling logic diagram is shown in Figure 16. This diagram defines the operation required to implement the selected contacting scheme. When expedient, secondary materials handling operations such as air suspension or chemical addition are included with the initial materials handling operation. The fourth digit of the 7-digit identification number is assigned by this diagram.

Water Control

Water control measures include all of the water containment and control operations necessary to prepare the lagoon for the selected initial materials handling process. Water control measures may include lagoon draining, dike construction, and perimeter lining. The fifth digit of the 7-digit identification number is assigned as indicated in Figure 17.

FIGURE 15. FEASIBLE CONTACTING SCHEMES – THIRD DIGIT

IS LAGOON BOTTOM PERMEABLE?

YES

IS WATER TABLE HIGH?

YES → ELIMINATE SOLID PHASE AND LAGOON → DO: SIDESTREAM CONTACTING

NO → CAN LEACHATE BE ISOLATED/COLLECTED?

YES → DO: SOLID PHASE LAGOON SIDESTREAM

NO → ELIMINATE SOLID PHASE AND LAGOON → DO: SIDESTREAM CONTACTING

NO

IS LATERAL PERCOLATION FEASIBLE?

YES → DO: SOLID PHASE LAGOON SIDESTREAM

NO → ELIMINATE SOLID PHASE → DO: LAGOON SIDESTREAM

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TABLE 3. APPLICABLE CONTACTING SCHEMES FOR CONVERSION PROCESSES

CONTACTING SCHEME	CONVERSION PROCESS
Solid Phase:	Chemical Reduction (inorganic or organic)
Liquid/Lagoon:	Chemical Reduction Alkaline Digestion Complexing-Hydrolysis Aerobic Biological Anaerobic Biological
Liquid/Sidestream:	Chemical Reduction Alkaline Digestion Complexing-Hydrolysis Gamma Irradiation Incineration Wet-Air Oxidation Aerobic Biological Anaerobic Biological

FIGURE 18. INITIAL MATERIALS HANDLING – FOURTH DIGIT

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FIGURE 17. WATER CONTROL MEASURES – FIFTH DIGIT
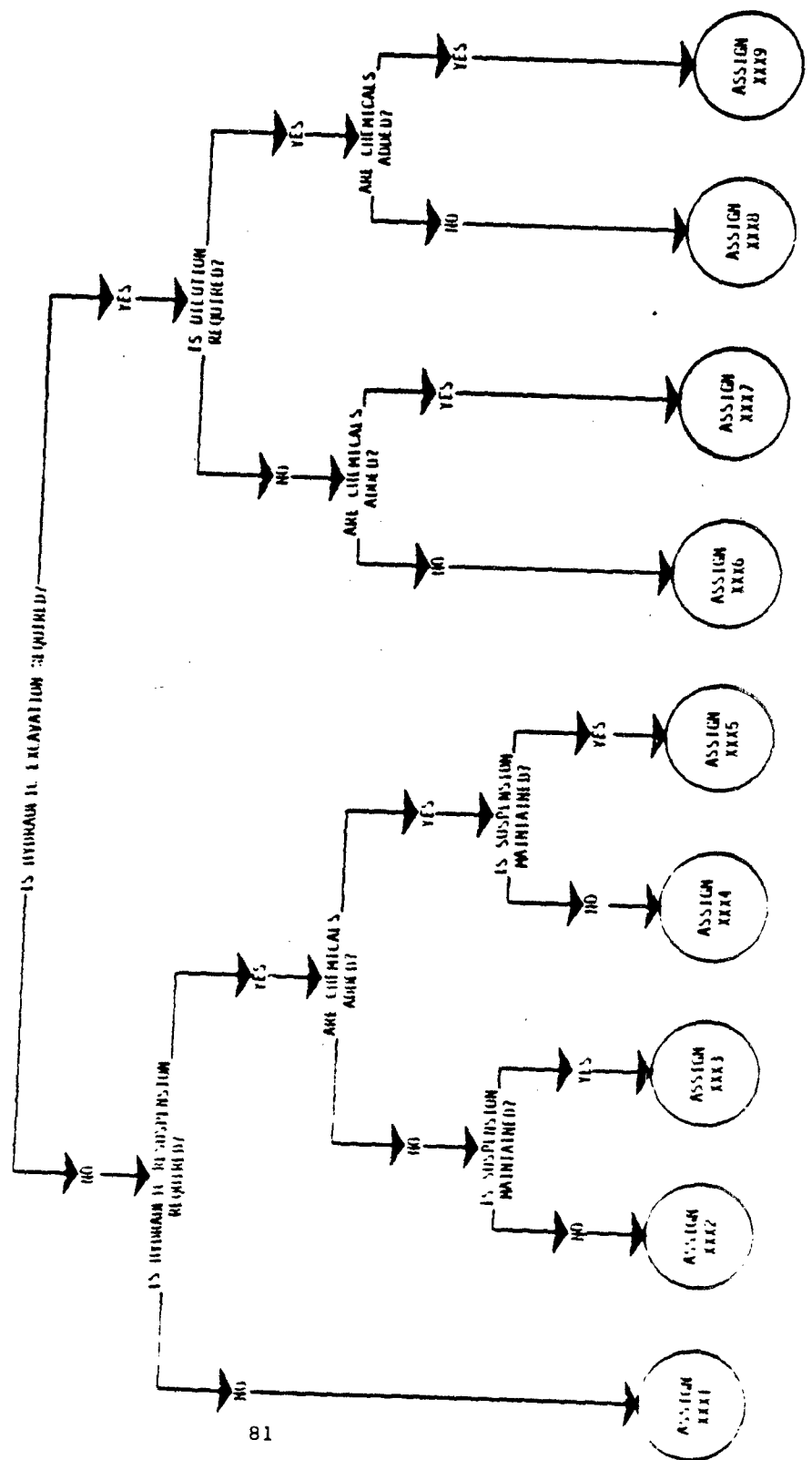
Basic Treatment Train

The basic treatment train logic diagram, shown in Figure 18, defines the treatment equipment (reactors, chemical addition, etc.) required for desensitization to take place in a selected conversion process. Excluded from this step is the consideration of equipment for materials handling or for treatment of desensitized wastes. The sixth digit of the 7-digit identification number is assigned as shown with this diagram.

Post-Desensitization Treatment

This logic diagram, shown in Figure 19, identifies the post-desensitization treatment (PDT) options. These include solid/liquid separation, neutralization, concentration/recovery, and discharge. The final digit of the 7-digit identification number is assigned by this logic diagram.

INITIAL MATERIALS HANDLING

The types of contacting schemes which are applicable to a proposed conversion process are identified in Table 3. The initial materials handling (IMH) procedures for implementing each contacting scheme can be classified as: insitu injection/recovery, insitu hydraulic resuspension and hydraulic excavation. The details of the proposed IMH processes are contained in Chapter 3 and Volume Two. A brief summation of these processes is presented below, and a summary of equipment requirements is presented in Table 4.

Insitu Injection/Recovery

With insitu injection/recovery, desensitization chemicals are applied to the lagoon sediment by a combination of well-point injection and surface flooding. Chemicals are withdrawn from the bottom of the sediment via extraction well points. Alternatively, a distribution piping system can be installed in the lagoon bed. Both the extracted and chemical makeup solutions can be recirculated until desensitization is achieved.

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FIGURE 18. BASIC EQUIPMENT TRAIN – SIXTH DIGIT

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FIGURE 19. POST DESENSITIZATION TREATMENT – SEVENTH DIGIT

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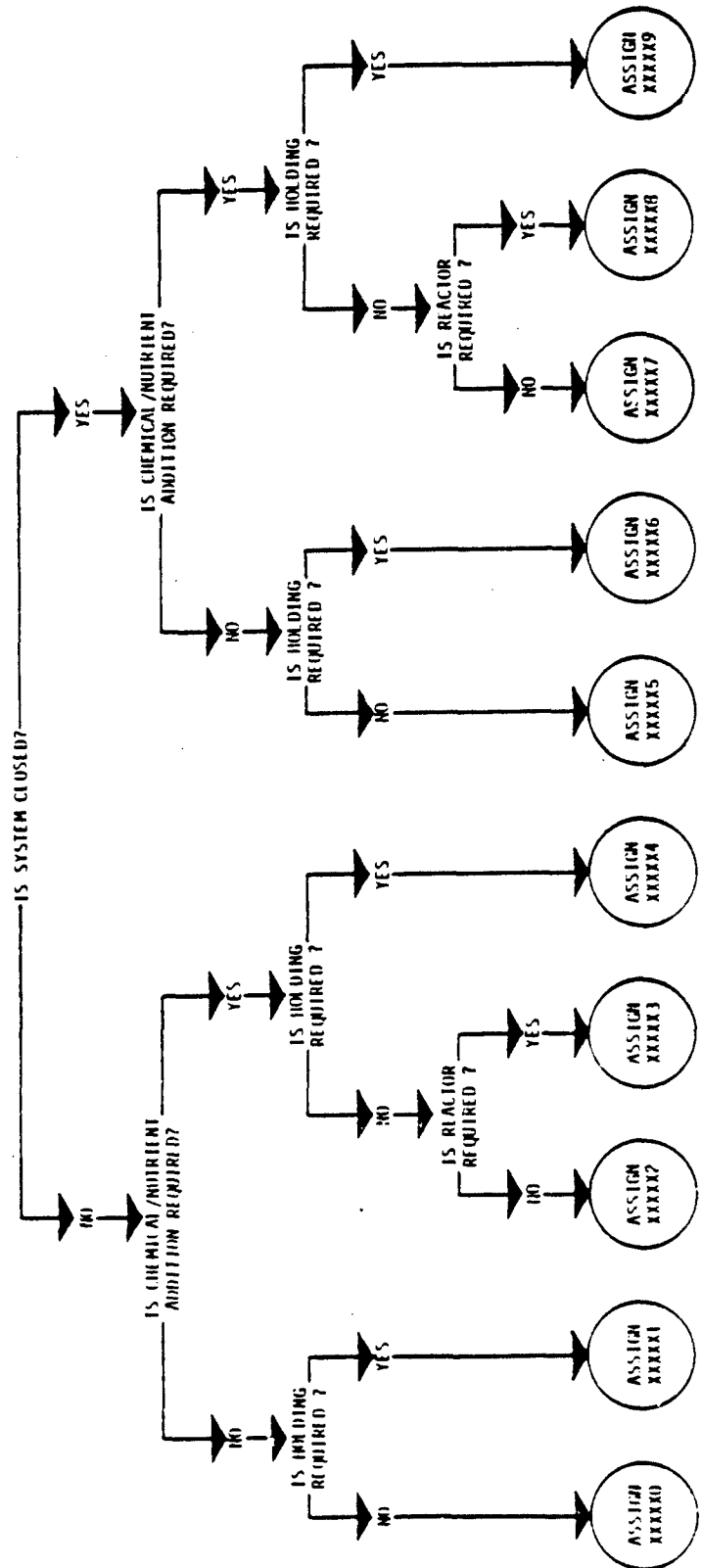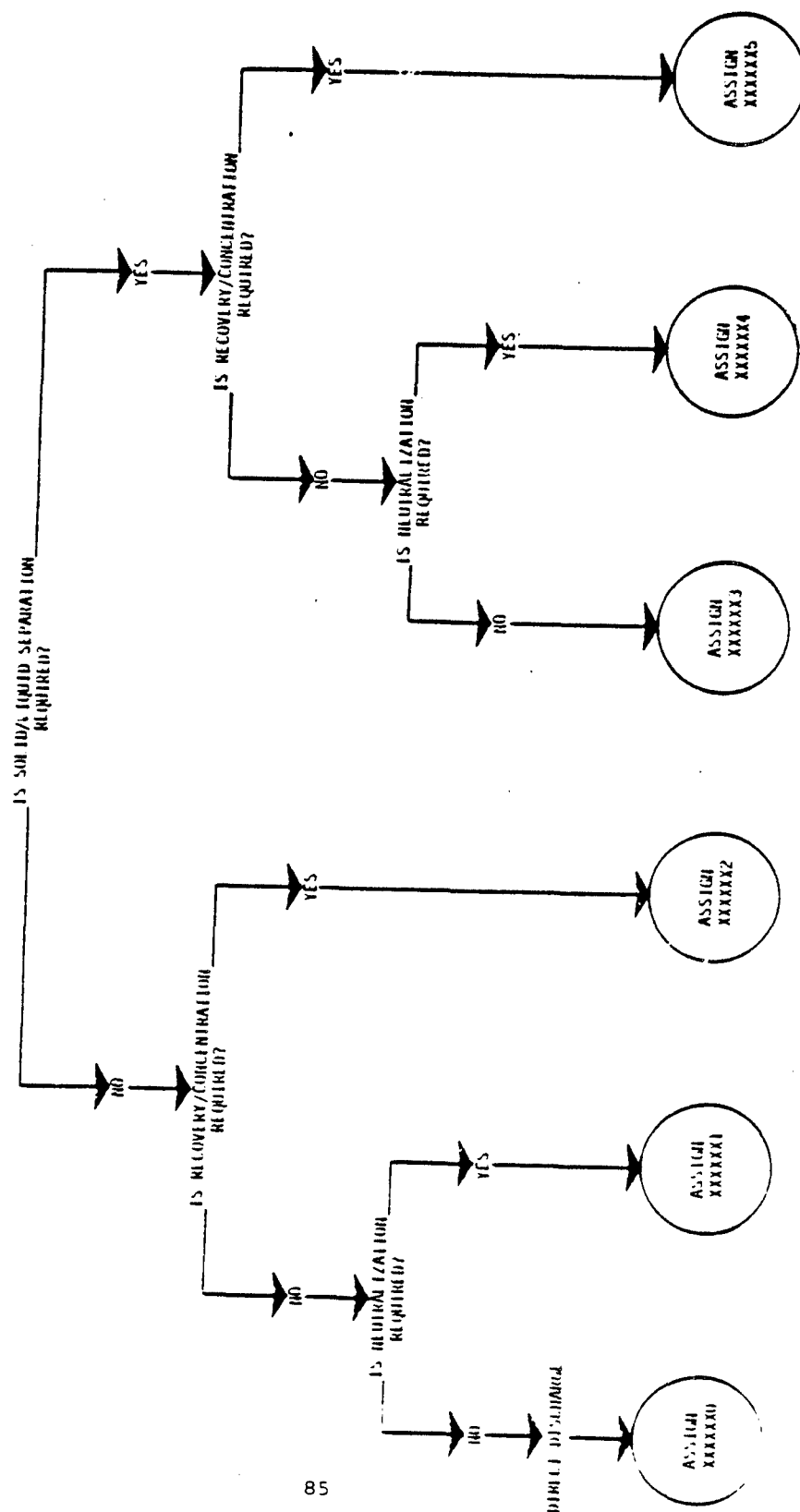
TABLE 4. EQUIPMENT LIST FOR THE INITIAL
MATERIALS HANDLING SUBALTERNATIVES

CONTACTING SYSTEM	TECHNIQUE	BASIC EQUIPMENT	OPTIONAL EQUIPMENT
Solid Phase	Injection/Recovery	Well Point Installation Equipment Injection, Recovery Pumping Holding/Surge Tanks	Water Control Equipment
Liquid Phase System (Lagoon/Sidestream)	Dredging Hydraulic Resuspension/Excavation	Dredge Cable-Winching	Auger Cage Assembly Crane (rental) Piping Remote Control Package Water Control Equipment Lagoon Suspension System
	Hydraulic Resuspension	Waterjet Device Waterjet Platform Pressure Pump Cable-Winching	Water Control Equipment Lagoon Suspension System

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Insitu Hydraulic Resuspension

Lagoon sediment is placed in suspension using a platform-mounted hydraulic cutting jet or dredging. If required, the suspension can be maintained by means of an air suspension (and mixing) system placed in the lagoon bottom to avert resettling of sediments. Either desensitization chemicals or water can be used as the medium for transferring energy to the suspension. The volume of liquid added to support the suspension is dependent upon both the sediment characteristics and the proposed conversion process.

Hydraulic Excavation

A Mudcat (Model SP 810) horizontal auger dredge or similar equipment is used to excavate the sediment. Water (if required) is added to the lagoon, and the dredge is lowered into the lagoon by a crane. The movement of the dredge is controlled by a cable-winching arrangement (Chapter 3). If desired, the dredge can be controlled remotely. An auger cage assembly is used when tramp metals other than UXO are present or a lagoon liner is in place.

DESENSITIZATION PROCESSING

The logic diagrams encompass the supporting secondary materials handling and separation processes as well as the proposed conversion processes and PDT methods. The number of available alternatives is greatly increased if PDT is also considered. However, because this report is directed to desensitization, only the basic alternatives will be evaluated. The PDT alternatives that were noted are identified as optional processes or equipment.

The complete descriptions of all the alternatives are presented in Volume Two and are summarized in this section. All processing equipment has been conceptualized to consider mobility, ease of assembly/disassembly, and modular technology.

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Chemical Processes

The chemical desensitization processes are reduction, complexing-hydrolysis, alkaline digestion and gamma irradiation. Alternatives for each process are selected through the use of the logic diagrams. The treatment trains indicated in the logic diagrams are summarized in Table 5 and illustrated in Figures 20 and 21. As shown, all chemical conversion processes are followed by similar options for PDT. Wastewaters containing desensitized sediments can be recycled directly in the same or an adjacent lagoon, discharged to a nearby wastewater treatment plant or treated by a separation and recovery process prior to reuse. Depending upon the contacting scheme, desensitized wastes can also be separated into liquid and solid fractions for purposes of PDT.

Chemical Reduction

Desensitization by chemical reduction can be accomplished using any of the three contacting schemes. Since a large variety of chemicals can be used as reductants, many chemical reduction alternatives can be defined. Although the choice of reductant will influence equipment size and design, the treatment trains of Table 5 are representative for most alternatives. All alternatives assume a 5-percent solids concentration in the sediment slurry. The basic alternative design and cost estimates were developed using sodium sulfide, hydrazine or formic acid as the reductant. Cost estimates for neutralization were based upon sodium sulfide.

Complexing-Hydrolysis

Desensitization by means of complexing-hydrolysis is performed in the liquid phase either insitu or as a sidestream in an adjacent vessel. Duoquad T-50 is the amino surfactant selected for the complexing of TNT and sodium hydroxide is used to adjust the pH of the sediment slurry. Desensitized effluent from the basic alternative can either be separated into liquid and solid fractions and/or neutralized prior to discharge. A concentration/recovery option was not cost-estimated in the comparative assessment of Chapter 5. A 5-percent solids concentration of surfactant is assumed in all alternatives.

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TABLE 5. SUMMARY OF ALTERNATIVE TREATMENT TRAINS

CONVERSION PROCESS	CONTACTING SCHEME	BASIC EQUIPMENT REQUIREMENT	OPTIONAL EQUIPMENT
Chemical Reduction	Solid Phase	Injection, Recovery Pumping; Chemical Holding, Make-up and Feed System	Neutralization Concentration/Recovery
	Liquid/Lagoon	Lagoon Mixing System; Chemical Holding, Make-up and Feed Systems	Closed Mixing System Air Scrubber Solid/Liquid Separation Neutralization Concentration/Recovery
	Liquid/Sidestream	Holding Tank or Lagoon Mixer; Reactor with Recirculation Loop; Chemical Holding, Make-up and Feed Systems	Neutralization Concentration/Recovery Air Scrubber Solid/Liquid Separation Closed Mixing System
Complexing-Hydrolysis	Liquid/Lagoon	Lagoon Mixing System; Chemical Holding, Make-up and Feed Systems	Neutralization Solid/Liquid Separation Lagoon Cover
	Liquid/Sidestream	Holding Tank or Lagoon Mixer; Reactor With Recirculation Loop; Chemical Holding, Make-up and Feed Systems	Neutralization Solid/Liquid Separation

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TABLE 5. SUMMARY OF ALTERNATIVE TREATMENT TRAINS (Continued)

CONVERSION PROCESS	CONTACTING SCHEME	BASIC EQUIPMENT REQUIREMENT	OPTIONAL EQUIPMENT
Alkaline Digestion	Liquid/Lagoon	Lagoon Mixing System; Chemical Holding, Make-up and Feed Systems	Neutralization Solid/Liquid Separation
	Liquid/Sidestream	Holding Tank or Lagoon Mixer; Closed Reacter With Recirculation Loop; Heat Exchanger; Chemical Holding, Make-up and Feed Systems	Neutralization Solid/Liquid Separation
Gamma Irradiation	Liquid/Sidestream	Holding Tank; Lagoon Mixer; Slurry Transfer Pump; Gamma Irradiation Unit	Neutralization Solid/Liquid Separation (if necessary to slurry) Chemical Holding, Make-up Feed Systems
Incineration	Liquid/Sidestream	Holding Tank or Lagoon Mixer; Incineration Unit	Solid/Liquid Separation Hydraulic Classifier Neutralization
Wet-Air Oxidation	Liquid/Sidestream	Holding Tank or Lagoon Mixer; Dilution/Chemical Addition; Mix Tank; Wet-Air Oxidation Unit	Neutralization
Aerobic Biological	Liquid/Lagoon	Lagoon Mix System; Chemical Holding, Make-up, and Feed System; Aeration System (Headers, Compressor)	Decant System Heat Exchanger

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TABLE 5. SUMMARY OF ALTERNATIVE TREATMENT TRAINS (Continued)

CONVERSION PROCESS	CONTACTING SCHEME	BASIC EQUIPMENT REQUIREMENT	OPTIONAL EQUIPMENT
	Liquid/Sidestream	Holding Tank or Lagoon Mixer; Closed Reactor With Recirculation Loop; Heat Exchanger; Chemical Holding, Make-up, and Feed System; Aeration System	Solid/Liquid Separation
Anaerobic Biological	Liquid/Lagoon	Lagoon Mix System; Air Scrubber; Chemical Holding Make-up, and Feed System	Decant System Heat Exchanger
	Liquid/Sidestream	Holding Tank or Lagoon Mixer; Closed Reactor(s) With Recirculation Loop, Heat Exchanger; Chemical Holding; Make-up and Feed System; Air Scrubber	Solid/Liquid Separation

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FIGURE 20. ALTERNATIVES FOR CHEMICAL PROCESSES

SOLID PHASE

LIQUID PHASE - LAGOON

LIQUID PHASE - SIDESTREAM

POST DESENSITIZATION ALTERNATIVES

① DIRECT REUSE (PARTIAL/TOTAL).	④ NEUTRALIZATION PROCESSES
② DISCHARGE TO AWTP/OTHER TREATMENT TRAINS.	⑤ SLURRY TO OTHER TREATMENT TRAINS.
③ RECOVERY/CONCENTRATION PROCESSES.	⑥ SOLIDS TO OTHER TREATMENT TRAINS.

LEGEND

POST DESENSITIZATION STREAM

DESENSITIZED STREAM

UNTREATED STREAM

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FIGURE 21. ALTERNATIVES FOR GAMMA IRRADIATION
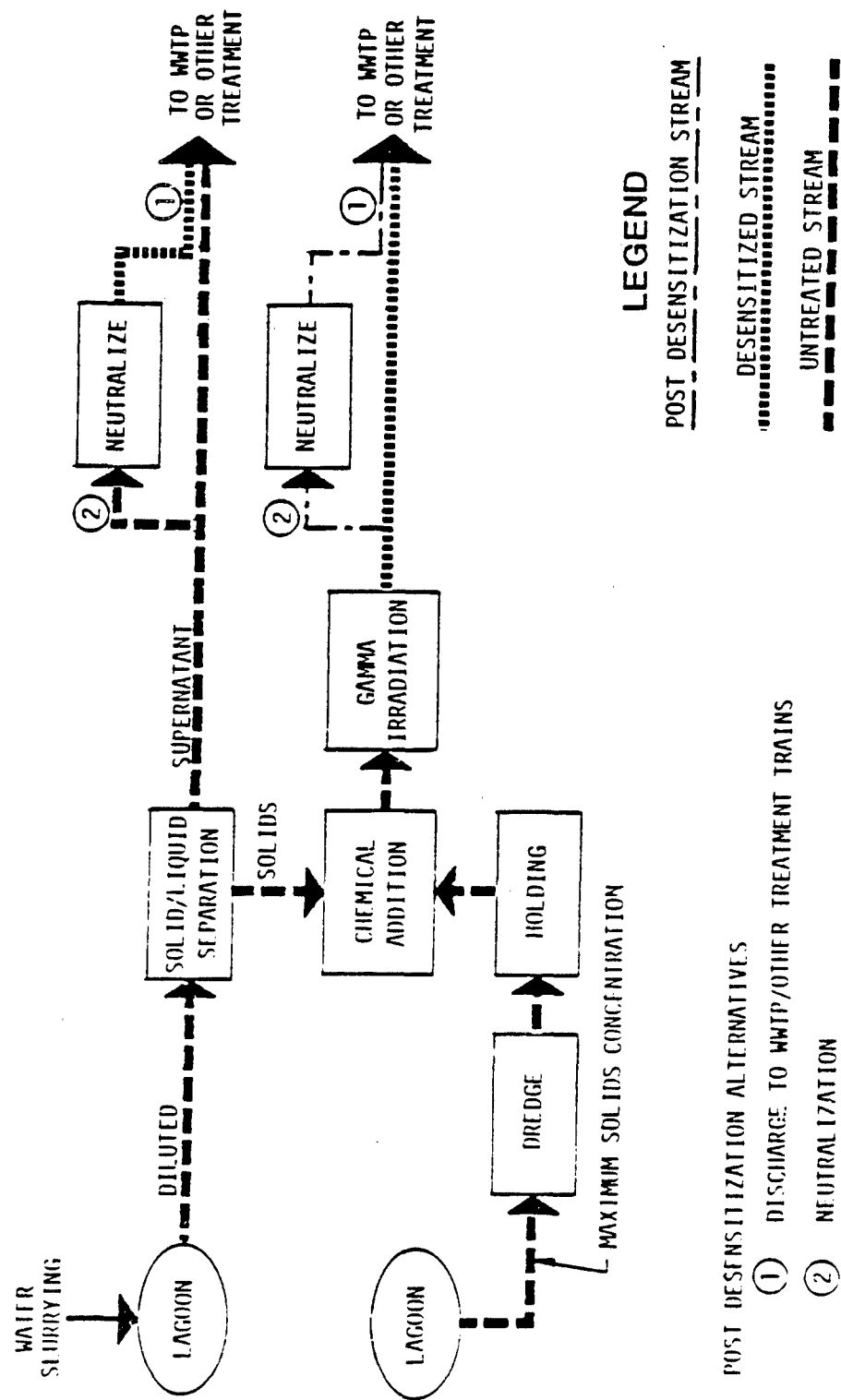
Alkaline Digestion

Desensitization by alkaline digestion is to be applicable only for nitrocellulose wastes. Either sodium hydroxide or ammonium hydroxide can be used for the digestion. If sodium hydroxide is used, the digestion can be accomplished insitu in the liquid phase or in an adjacent sidestream reactor. If ammonium hydroxide is used, the digestion must be performed in an adjacent sidestream reactor. An elevated temperature is assumed to be required to minimize volume for digestions performed in the sidestream reactor and it is assumed that insitu digestion can be performed at ambient temperature. If feasible, the sediment is excavated and treated with a minimum of dilution. Desensitized effluent from the basic alternative can be separated into liquid and solid fractions and/or neutralized prior to discharge.

Gamma Irradiation

Desensitization by gamma irradiation is performed in an adjacent sidestream reactor. If feasible, the lagoon sediment is excavated with a minimum of dilution and pretreated by chemical addition. Depending upon the character of the lagoon, it may be necessary to slurry the sediment prior to excavation. Solid-liquid separation is then provided for pretreatment; the desensitized slurry can be neutralized or discharged directly.

Thermal Processes

The thermal desensitization processes are incineration and wet-air oxidation. The basic alternative for both processes should result in a higher degree of treatment than should be attainable with the chemical or biological conversion processes. In this regard, incineration is indicated as the baseline method against which all other methods are to be compared. The treatment trains defined from use of the logic diagrams are listed in Table 5, illustrated in Figure 22 and discussed below.

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FIGURE 22. ALTERNATIVES FOR THERMAL PROCESSES
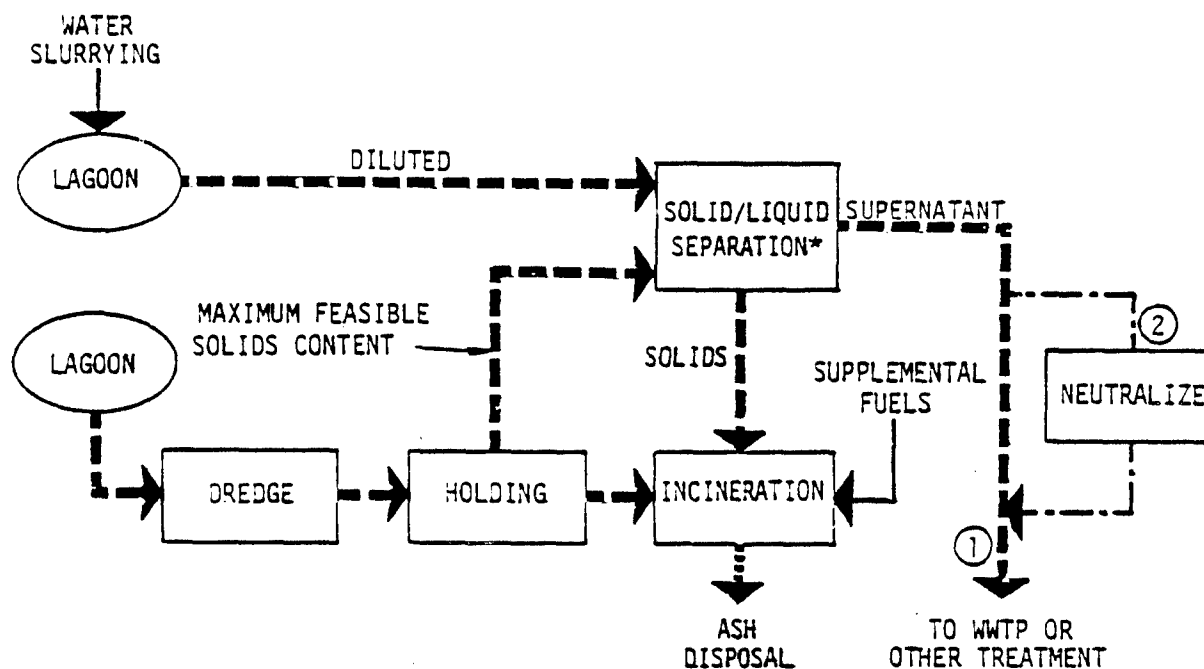
INCINERATION
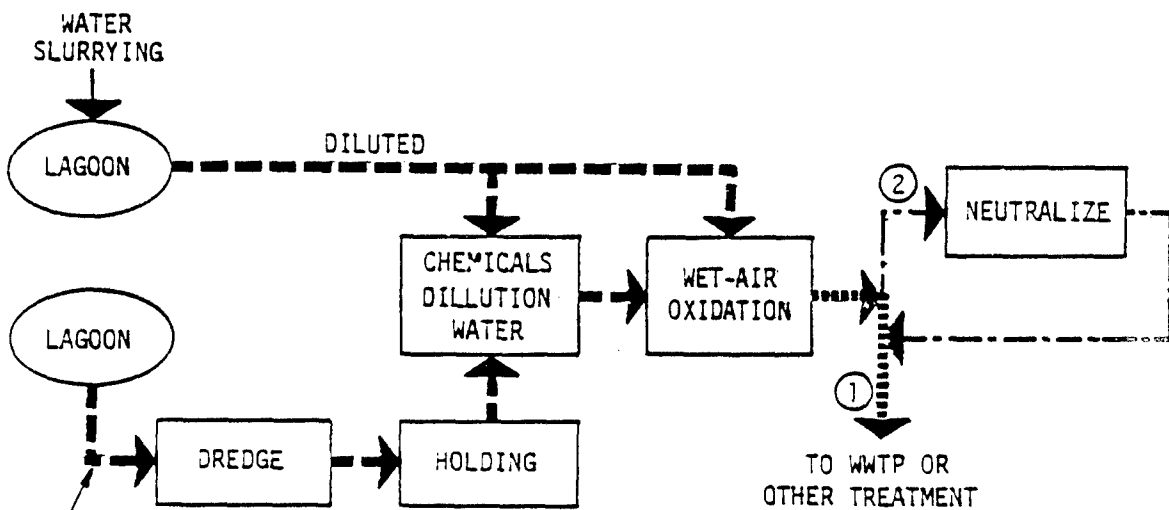
WET-AIR OXIDATION

POST DESENSITIZATION ALTERNATIVES

① DISCHARGE TO WWTP/OTHER TREATMENT TRAINS

② NEUTRALIZATION PROCESSES

* INCLUDES HYDRAULIC CLASSIFICATION

LEGEND

POST DESENSITIZATION ST

DESENSITIZED STREAM

UNTREATED STREAM

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Incineration

The lagoon sediment is excavated with a minimum of dilution (or none if feasible) and transferred to a holding tank/lagoon. Hydraulic classification or dewatering can be provided prior to incineration. The wastewater effluent from the solids-liquid separation can be neutralized or discharged directly. If available, waste oil or solvent can be used to satisfy supplemental fuel requirements so long as regulations for combustion of the materials are met.

Wet-air Oxidation

Desensitization by the wet-air oxidation process is done in the liquid phase in a sidestream reactor. The lagoon sediment is assumed to be diluted to a 5-percent solids concentration and treated by chemical addition prior to oxidation. The desensitized slurry can be neutralized prior to discharge.

Biological Processes

The biological desensitization processes are aerobic and anaerobic digestion. The treatment trains defined by the logic diagram are summarized in Table 5 and shown in Figure 23. The treatment trains are essentially the same for both processes; domestic sewage sludge is assumed to be used as a carbon, nutrient and alkalinity source.

Aerobic Treatment

Desensitization by aerobic biological treatment can be provided only in the liquid phase, either insitu in batch mode or in an adjacent reactor(s) in a batch or continuous flow mode. This process is only applicable for the desensitization of TNT, and it is further assumed that the biotransformation occurs only on the soluble TNT fraction. Toxic metals, if present, are removed by sulfide precipitation. The lagoon sediment is diluted to a 5-percent solids concentration and the appropriate

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FIGURE 23. ALTERNATIVES FOR BIOLOGICAL PROCESSES
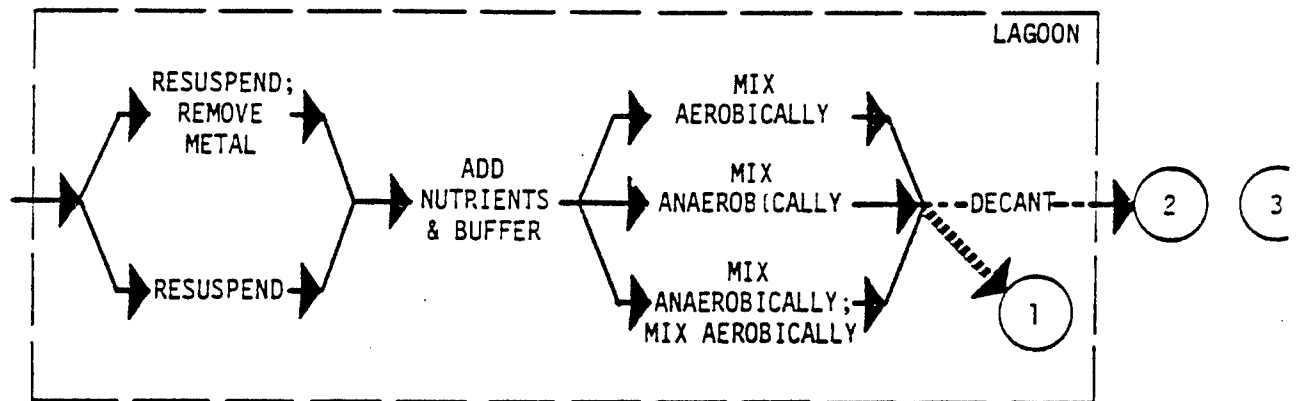
LIQUID PHASE - LAGOON
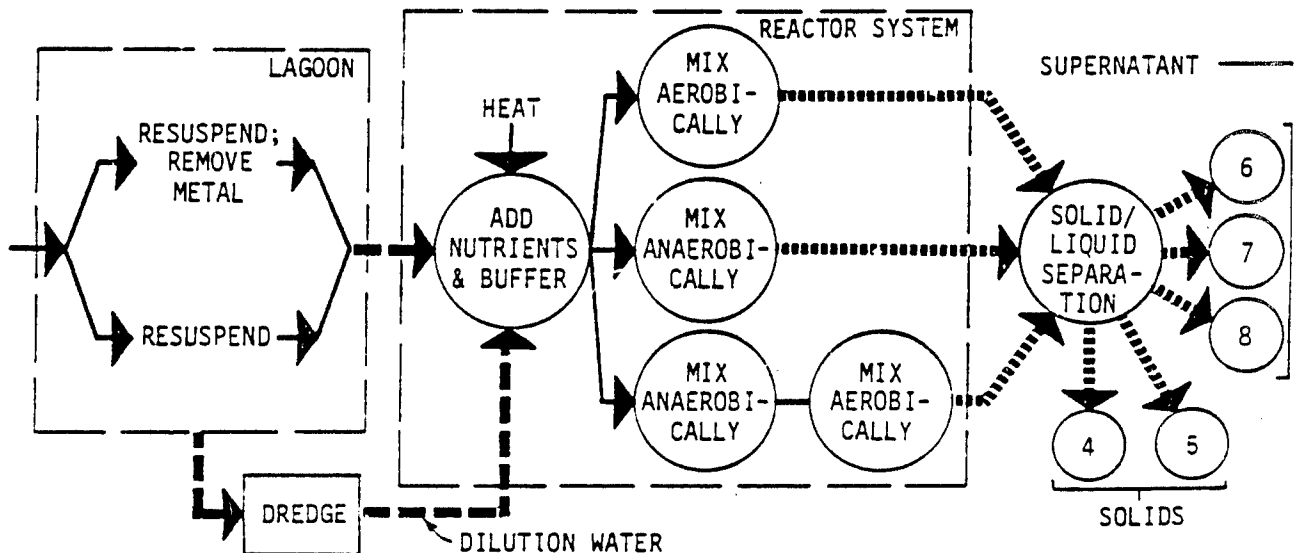
LIQUID PHASE - SIDESTREAM

POST-DESENSITIZATION ALTERNATIVES

(1) RETAIN SLURRY IN LAGOON
(2) RETAIN SOLIDS IN LAGOON; TRANSFER SUPERNATANT TO OTHER TREATMENT TRAIN
(3) RETAIN SOLIDS IN LAGOON; TRANSFER SUPERNATANT TO ANOTHER LAGOON AS MAKEUP
(4) RETURN SPENT SOLIDS TO LAGOON
(5) TRANSFER SPENT SOLIDS TO OTHER TREATMENT TRAIN
(6) TRANSFER SUPERNATANT TO LAGOON
(7) TRANSFER SUPERNATANT TO OTHER TREATMENT TRAIN
(8) TRANSFER SUPERNATANT TO ANOTHER LAGOON

LEGEND

POST DESENSITIZATION STREAM

DESENSITIZED STREAM

UNTREATED STREAM

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nutrients, seed culture and buffer solutions are added prior to treatment. The slurry is then mixed and aerated until desensitization is achieved. Heat addition, if cost effective, increases reaction rates thereby reducing detention time and reactor volume. Heat addition is assumed for the continuous sidestream reactor system. The desensitized slurry can be discharged, decanted and stabilized or treated by solid-liquid separation prior to discharge.

Anaerobic Treatment

Desensitization by anaerobic biological treatment can also be provided in the liquid phase, either insitu in batch mode or in an adjacent reactor(s) in batch or continuous mode. Equipment requirements are the same as for the aerobic process with the exception of the aeration system. Heat addition is assumed for the continuous sidestream reactor system. Resuspension of the sediment is accomplished on an intermittent basis by a modified dredge. The dredge intake and discharge are positioned below the water surface to minimize surface disturbance. Because the dredge is floated on the surface, a lagoon cover is infeasible. Nonetheless, anaerobic conditions analogous to those attained in facultative (anaerobic) ponds are assumed to prevail. The post-desensitization options are the same as for the aerobic process.

CHAPTER 5

COST ESTIMATES

The preceding chapter illustrates the combinations of initial materials handling, conversion, secondary materials handling and post-desensitization treatment processes and operations that can be defined. Conceivably there are a multitude of feasible alternatives for each specific lagoon - a circumstance that would allow considerable flexibility in selecting a preferred approach. However, of the many factors that would dictate a preferred choice, cost is among the more important.

The alternatives as described in Chapter 4 are characterized to a very preliminary stage. With continued development and the aid of a computer program, cost estimates could be developed for each alternative applied to each lagoon situation and then a computerized search conducted to define the least-cost alternative(s) for each lagoon. From this benchmark, a least-cost strategy, i.e., combination of alternatives, could be defined by computer search for each installation and ultimately for the defense establishment. Such an analysis could be accompanied by the capability to estimate equipment and personnel requirements and deployment, and local and system-wide costs for complete systems tailored to the needs of each lagoon and installation.

Although such an inquiry cannot be made at this time, and perhaps not for another year or two, the results of the preceding chapter can be combined with unit cost parameters to develop preliminary estimates of costs for each type of desensitization process. This approach has been used to develop cost estimates for alternatives representing each conversion process, the applicable contacting schemes for each conversion process, and a representative post desensitization treatment option.

The cost parameters were developed on a unit process basis to facilitate the compilation of cost estimates. Modular technology was assumed to allow the mobility and flexibility required for repeated

transportation, assembly and disassembly at the various lagoon locations. This approach also allows the addition or deletion of units as required by variations in lagoon size. Whenever possible, modular units were sized for transportation on standard truck trailers.

The cost estimates in this chapter were developed to be used in conjunction with the other performance measures for evaluation of the various alternatives in Chapter 6. The cost estimates reflect the constraints and limitations previously outlined and are, at best, only relative indications of cost for the various desensitization alternatives. Extensive developmental work will be required before the cost estimates can be improved, particularly with respect to the costs of safety procedures and environmental permits attendant to any installation.

CASE EXAMPLES

In order to provide a setting for the application of the technologies and development of cost estimates, eight representative lagoon case examples were defined using available characterization data (ESE, 1982). The design basis and cost estimates that follow later in this chapter were based upon a "standard" lagoon scenario whenever possible because it was not expedient (or necessary) to examine all alternatives for purposes of this study. This standard lagoon is designated as "Case One" below. The effects of all of the selected case examples on cost and the other performance measures are compared and contrasted in Chapter 6.

The eight lagoon case examples are summarized in Table 6 and described below.

Case One

Case One has the following assumed characteristics:

o   Size: 100 feet x 150 feet x 9 feet depth
o   Depth of sediment: 1 foot
o   Sediment moisture content: 50 percent

TABLE 6. SELECTED LAGOON CASE EXAMPLES

CASE	TYPE OF SOIL/SEDIMENT SAND/GRAVEL	CLAY	LINER [b]	TNT	RDX	NC	<5%	>5%	TOXIC METALS
1	x		x	x	x			x	
2	x		x	x	x		x		
3	x			x	x			x	
4		x	x	x	x			x	
5	x		x	x	x			x	
6 [a]	x		x	x	x		x		x
7	x		x	x	x	x		x	
8	x		x	x				x	

Notes:

a   All lagoons are "standard size" (100 ft x 150 ft) except that for Case 6, which is 10-fold larger.

b   "Liner" connotes the presence of either a natural clay soil acting as an impermeable barrier, or a manmade liner.

- o Volume of sediment: 15,000 ft^3
- o Dry weight of sediment: 600 tons
- o Explosives content of sediment (dry weight basis):

    10% TNT; 5% RDX
- o Soil/sediment type, sand and gravel
- o Dry lagoon
- o Tramp metal and unexploded ordnance (UXO) are not present
- o Wastewater treatment plant available
- o Intact lagoon liner

Additional assumptions are that the lagoon does not require diking or other water control measures, is accessible by truck, only one lagoon is present at the site and water, electricity and steam are available within a reasonable distance or can be provided.

Case Two

Case Two is identical to Case One with the exception that the explosives content of the sediment (dry weight basis) is assumed to be 1% TNT and 0.5% RDX.

Case Three

Case Three is identical to Case One with the exception that the lagoon is unlined and that a high water table is present.

Case Four

Case Four is identical to Case One with the exception that the soil and sediments have a high clay content.

Case Five

Case Five is identical to Case One with the exception that heavy metals are present and a sediment dilution of 5 to 10% is required for hydraulic excavation.

Case Six

Case Six consists of a lagoon that is assumed to be 10-fold larger than used in Case One. TNT and RDX are present at a dry weight content of one percent and 0.5 percent respectively. All other characteristics are identical to those assumed for Case One.

Case Seven

Case Seven consists of a lagoon which has been dedicated to the disposal of nitrocellulose processing wastewaters. The nitrocellulose content in the sediment is six percent on a dry weight basis. Phthalates (used for gelatinizing) are also assumed to be present, but no other explosives or propellants are in the sediment. All other characteristics are identical to those for Case One.

Case Eight

Case Eight is identical to Case One with the exception that only TNT (and not RDX) is assumed to be present in the lagoon.

BASIS OF ESTIMATES

Capital Costs

Unit capital costs and a complete design basis are presented in Volume Two for all equipment required for initial materials handling, secondary materials handling, separation and conversion processes. Equipment capital costs are based upon vendor quotations or normal estimating procedures. All costs were adjusted to a December 1982 basis. Costs were calculated on a per-lagoon basis by estimating the number of lagoons that could be treated during the life of the equipment using the lagoon size and volume as defined above for Case One. The number of lagoons that can be treated per year was estimated at eleven, unless otherwise determined by the nature of the conversion process. Estimates of useful life for equipment items were based upon vendor information or standard estimating procedures.

Each unit cost includes allowances for instrumentation, wiring, piping and valving. Allowances for such were either based upon a percentage of the capital cost that was determined by the type and complexity of the unit or on individual cost estimates.

In providing these cost estimates, an effort was made to furnish a realistic and representative estimate for implementation of the desensitization alternatives. However, there are specific site and indirect costs which are not generalized. These costs include:

- o Environmental permit at all governmental levels
- o Spare parts and backup equipment
- o Freight and transportation charges
- o Yard improvements (site clearing, roadways, etc.)
- o Service facilities, steam, cooling water
- o Operating personnel, travel and living expenses
- o Construction financing
- o Insurance and taxes

A 15-percent contingency was included for all alternatives. Site preparation, installation and assembly costs, normally treated as first cost components, were assumed to be operating costs due to the changing locational nature of the operation.

Operating Costs

Operating costs were estimated for each alternative on a per-lagoon basis. Costs were also estimated on a unit process basis whenever possible. Unit operating costs and a complete design basis for each alternative are included in Volume Two. All costs were adjusted to a December 1982 basis. Maintenance and installation (site preparation and assembly) were based upon either a percentage of capital cost determined by the type and complexity of the unit or upon an individual cost estimate. Labor costs were determined by the amount of time required to mobilize, implement and demobilize the system at a lagoon. The burdened salary basis (includes overhead) for estimation of labor costs varied from $20/hour for

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a mechanic to $44/hour for a supervisor. Electrical power costs were estimated for the installed horsepower in each system, assuming a 60-percent efficiency and electricity costs at $0.08/kwh.

With the exception of the sidestream biological alternatives, utility costs were estimated at $0.06/1000 gallons of cooling water and $0.80/1000 pounds of saturated steam at atmospheric pressure. These estimates were obtained from standard costing information (Peters and Timmerhaus, 1980). The availability of these utilities at the lagoon is unknown; however, it turned out that the cost of these items for most alternatives is small in comparison to other operating costs. If necessary, electricity can be substituted for steam and cooling water can be pumped to the lagoon.

In the case of the sidestream biological alternatives, large amounts of heat are required; therefore, the estimates of heating costs are critical to the evaluation of these alternatives. Of the available heat addition methods, the use of low pressure steam from portable gas-fired generators was chosen for cost estimation. It was assumed that one generator is supplied with each reactor, however, in most situations a single generator would be used to supply all reactors.

Chemical dosages are based upon data obtained during the literature search and site survey or estimated on a theoretical basis. Actual chemical requirements may differ significantly and must be determined by laboratory/pilot testing. Chemical dosage assumptions are included in the design basis for each alternative. In cases where more than one chemical may be used, representative chemicals were costed. Chemical costs were obtained from the Chemical Marketing Reporter (January 3, 1983) or through vendor quotations.

COST ESTIMATES

The capital and operating cost estimates are developed on a line item, per-lagoon basis and presented in Tables 7 to 18. The chemical costs used to develop the operating cost estimates are presented in Table 19. A summary of capital and operating costs for all the situations evaluated is

presented in Table 20. The costs of incineration were updated from the ARC report (1982). Although incineration is the baseline alternative, all costs are ranked by comparison to each other, not to incineration (Chapter 6).

The estimates developed pertain primarily to Case One and are presented as follows:

Table	Technology	Case
7	Solid phase chemical reduction	One
8	Liquid/lagoon chemical reduction	One
9	Liquid/sidestream chemical reduction	One
10	Liquid/lagoon complexing-hydrolysis	One
11	Liquid/sidestream complexing-hydrolysis	One
12	Liquid/lagoon alkaline digestion	Seven
13	Liquid/sidestream alkaline digestion	Seven
14	Liquid/sidestream gamma irradiation	One
15	Liquid/sidestream incineration	One
16	Liquid/sidestream wet-air oxidation	One
17	All aerobic biological	Eight
18	All anaerobic biological	One

Capital Costs

The capital cost estimates are summarized in Table 20. It is apparent from this summary that the solid phase contacting method is 7 to 50-fold more costly than either the liquid/lagoon or liquid/sidestream method. As is evident from inspection of Table 7, that the well injection system is an extremely costly element in the solid phase contacting method. However, in some cases the benefits of not having to disturb the soil/sediment may more than offset the cost.

The capital costs of the liquid/sidestream thermophillic biological treatment alternatives vary from $288,300 to $419,000 per lagoon and are 6 to 9-fold greater than those for the ambient temperature liquid/lagoon

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TABLE 7. COST ESTIMATES - SOLID PHASE CHEMICAL REDUCTION (CASE ONE)

ALTERNATIVE	OPERATION	ITEM	BASIS	COST CAPITAL ($/lagoon)	COST OPERATING ($/lagoon)
Basic	Initial Materials Conversion	Well Injection System	30 days	923,940	336,700
		Chemical Feed	2 days	860	50
		Hydrazine-Hydrate		-	85,550
		Sodium Sulfide		-	(52,320)
		Formic Acid		-	(167,256)
		Subtotal		924,800	422,250
		Contingency (15%)		138,700	-
		TOTAL		1,063,500	422,250
Optional	Post-Desensitization Treatment	Neutralization	50 gpm	125	50
		Chemical Feed	8 gpm	120	25
		Hydrogen Peroxide		-	22,630
		Subtotal		250	22,705
		Assembly, Site (15%)			40
		Contingency (15%)		40	-
		TOTAL		290	22,750

Note: ( ) denotes cost for an alternate chemical

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TABLE 8. COST ESTIMATES - LIQUID/LAGOON CHEMICAL REDUCTION (CASE ONE)

ALTERNATIVE	OPERATION	ITEM	BASIS	COST CAPITAL ($/lagoon)	OPERATING ($/lagoon)
Basic	Initial Materials	Filling-Dredging	17 days	11,000	7,400
	Secondary Material	Suspension System	2 days	12,700	950
	Conversion	Chemical Feed		860	50
		Hydrazine		–	85,550
		Sodium sulfide		–	(52,320)
		Formic Acid		–	(167,256)
		Subtotal		24,560	93,950
		Contingency (15%)		3,680	–
		TOTAL		28,240	93,950
Optional	Post-Desensitization	Lagoon Suspension	10 days	–	4,700
	Treatment	Solid/Liquid Separaton	100 gpm	13,200	300
		Neutralization	100 gpm	250	100
		Chemical Feed		240	50
		Hydrogen Peroxide		–	22,630
		Subtotal		13,690	27,780
		Assembly, Site (15%)			2,050
		Contingency (15%)		2,050	–
		TOTAL		15,740	29,830

Note: ( ) denotes cost for an alternate chemical

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TABLE 9. COST ESTIMATES - LIQUID/SIDESTREAM CHEMICAL REDUCTION (CASE ONE)

ALTERNATIVE	OPERATION	ITEM	BASIS	COST	
				CAPITAL ($/lagoon)	OPERATING ($/lagoon)
Basic	Initial Materials	Filling-Dredging	17 days	11,000	7,400
	Secondary Materials	Suspension System	20 days	12,700	9,470
	Conversion	Slurry Pump	50 gpm	550	180
		Reactor		3,360	540
		Chemical Feed System	13 gph	240	50
		Hydrazine-Hydrate		–	85,550
		Subtotal		27,850	103,190
		Assembly, Site Work (15%)			4,200
		Contingency (15%)		4,200	–
		TOTAL		32,050	107,400
Optional	Post-Desensitization	Solid/Liquid Separation	50 gpm	6,600	200
	Treatment	Neutralization		125	50
		Chemical Feed	8 gph	120	25
		Hydrogen Peroxide		–	22,630
		Subtotal		6,845	22,905
		Assembly (15%)		–	1,030
		Contingency (15%)		1,030	–
		TOTAL		7,857	23,930

TABLE 10. COST ESTIMATES —LIQUID/LAGOON COMPLEXING-HYDROLYSIS (CASE ONE)

ALTERNATIVE	OPERATION	ITEM	BASIS	COST CAPITAL ($/lagoon)	OPERATING ($/lagoon)
Basic	Initial Materials	Filling-Dredging	17 days	11,000	7,400
	Secondary Materials	Suspension System	2 days	12,700	946
	Conversion	Chemical Feed		660	50
		Surfactant		-	60,210
		Sodium Hydroxide		-	480
		Subtotal		24,560	69,100
		Contingency (15%)		3,680	-
		TOTAL		28,240	69,100
Optional	Post-Desensitization	Lagoon Suspension	10 days	-	4,700
	Treatment	Solid/Liquid Separation	100 gpm	13,200	300
		Neutralization	100 gpm	250	100
		Chemical Feed	0.6 gph	120	25
		Sulfuric Acid		-	40
		Subtotal		13,570	15,165
		Assembly, site (15%)		-	2,040
		Contingency (15%)		2,040	-
		TOTAL		15,610	7,200

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TABLE 11. COST ESTIMATES - LIQUID/SIDESTREAM COMPLEXING - HYDROLYSIS (CASE ONE)

ALTERNATIVE	OPERATION	ITEM	BASIS	CAPITAL ($/lagoon)	OPERATING ($/lagoon)
Basic	Initial Materials	Filling-Dredging	17 days	11,000	7,400
	Secondary Material	Suspension System	20 days	12,700	9,470
	Conversion	Slurry Pump	50 gpm	550	180
		Reactor		3,360	540
		Chemical Feed	(24 gph)	240	50
		Surfactant		-	60,210
		Sodium Hydroxide		-	480
		Subtotal		27,850	78,330
		Assembly, Site (15%)		4,200	4,200
		Contingency (15%)			
		TOTAL		32,050	82,530
Optional	Post-Desensitization	Solid/Liquid Separation	50 gpm	6,600	200
	Treatment	Neutralization	50 gpm	125	50
		Chemical Feed System	0.3 gph	120	25
		Sulfuric Acid		-	40
		Subtotal		6,850	350
		Assembly (15%)		-	1,030
		Contingency (15%)		1,030	-
		TOTAL		7,880	1,350

TABLE 12. COST ESTIMATES - LIQUID/LAGOON ALKALINE DIGESTION (CASE SEVEN)

ALTERNATIVE	OPERATION	ITEM	BASIS	CAPITAL ($/lagoon)	OPERATING ($/lagoon)
Basic	Initial Materials	Dredging	10 days	1,280	2,320
	Secondary Material Conversion	Suspension System	5 days	12,700	2,370
		Chemical Feed		860	50
		Sodium Hydroxide		-	15,290
		Subtotal		14,840	20,030
		Contingency (15%)		2,230	-
		TOTAL	-	17,070	20,030
Optional	Post-Desensitization Treatment	Suspension System	2 days	-	20,030
		Solid/Liquid Separaton	50 gpm	6,600	950
		Neutralization	50 gpm	125	200
		Chemical Feed	2 gpm	860	50
		Sulfuric Acid		-	50
		Subtotal		7,585	2,340
		Assembly, Site (15%)		-	3,590
		Contingency (15%)		1,140	1,140
		TOTAL		8,725	4,730

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TABLE 13. COST ESTIMATES - LIQUID/SIDESTREAM ALKALINE DIGESTION (CASE SEVEN)

ALTERNATIVE	OPERATION	ITEM	BASIS	COST CAPITAL ($/lagoon)	COST OPERATING ($/lagoon)
Basic	Initial Materials	Dredging	10 days [a]	1,280	2,320
		Suspension System	1 day [a]	12,700 [b]	470 [c]
		Slurry Pump		860	65
		Reactor		1,860	540
		Heat Exchanger		350	70
		Chemical Feed		860	50
		Sodium Hydroxide		–	15,290
		Ammonium Hydroxide		–	(47,100)
		Subtotal		17,900	18,800
		Assembly, Site (15%)		2,670	2,650
		Contingency (15%)			–
		TOTAL		20,600	21,500
Optional	Post-Desensitization Treatment (NaOH)	Solid/Liquid Separation	100 gpm	13,200	300
		Neutralization	100 gpm	250	100
		Chemical Feed	4 gpm	860	50
		Sulfuric Acid			2,340
		Subtotal		14,310	2,790
		Assembly, Site (15%)		–	2,150
		Contingency, (15%)		2,150	–
		TOTAL		16,460	4,940

Note:
a   4 days if NH$_4$OH is used at 25 gpm flowrate

b $550 if NH$_4$OH is used at 25 gpm flowrate

c $1,900 if NH$_4$OH is used at a 25 gpm flowrate

    ( ) denotes cost for an alternate chemical

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TABLE 14. COST ESTIMATES - LIQUID/SIDESTREAM GAMMA IRRADIATION (CASE ONE)

ALTERNATIVE	OPERATION	ITEM	BASIS	CAPITAL ($/lagoon)	OPERATING ($/lagoon)
Basic	Initial Materials	Dredging	10 days	1,280	2,320
	Secondary Material	Suspension System	6 days	12,700	2,840
		Slurry Pump	14 gpm	550	100
		Gamma Irradiation System		7,000	-
		Maintenance		-	260
		Labor		-	23,500
		Electricity		-	870
		Irradiating Source		-	350
		Installation		-	1,050
		Subtotal		21,530	31,300
		Contingency (15%)		3,230	-
		TOTAL		24,800	31,300

TABLE 15. ESTIMATES - LIQUID/SIDESTREAM INCINERATION (CASE ONE)

ALTERNATIVE	OPERATION	ITEM	BASIS	CAPITAL COST ($/lagoon)	OPERATING ($/lagoon)
Basic	Initial Materials	Dredging	10 days	1,280	2,320
	Secondary Material	Suspension System	25 days	12,700	11,800
		Slurry Pump		550	200
	Conversion	Incineration System		7,700	-
		Labor		-	28,500
		Fuel Oil #2		-	19,600
		Electricity		-	930
		Maintenance		-	390
		Installation		-	390
		Subtotal		22,230	-
		Contingency (15%)		3,350	-
		TOTAL		25,600	64,130

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TABLE 16. COST ESTIMATES - LIQUID/ SIDESTREAM WET-AIR OXIDATION (CASE ONE)

ALTERNATIVE	OPERATION	ITEM	BASIS	COST CAPITAL ($/lagoon)	OPERATING ($/lagoon)
Basic	Initial Materials	Filling-Dredging	17 days	11,000	7,400
	Secondary Material	Suspension System	50 days	12,700	22,720
		Slurry Pump		550	390
	Conversion	Wet Air Oxidation System		86,540	-
		Labor		-	50,000
		Electricity		-	15,400
		Chemicals		-	1,060
		Cooling Water		-	450
		Maintenance		-	2,600
					4,330
		Installation			
		Subtotal		110,790	-
		Contingency (15%)		16,600	-
		TOTAL		127,400	104,350

TABLE 17. COST ESTIMATES - LIQUID/LAGOON AEROBIC BIOLOGICAL TREATMENT (CASE EIGHT)

ALTERNATIVE	OPERATION	ITEM	BASIS	CAPITAL ($/lagoon)	OPERATING ($/lagoon)
Basic	Initial Materials	Dredging			
	Secondary Materials	Air-Suspension System	30 days	11,000	7,400
	Conversion	Sludge Feed System	1.7 GPM	12,700	14,200
				860	50
		Subtotal		24,560	21,650
		Contingency (15%)		3,680	-
		TOTAL		28,240	21,650
Sidestream (Thermophilic)	Initial Materials	Dredging		11,000	7,400
	Secondary Materials	Air-Suspension System	32 days	12,700	14,200
	Conversion	Reactor:	12,000 gal		
		Closed Reactor		3,650	-
		Preheater		430	-
		Heat Exchanger		120	-
		Sludge Feed System		150	-
		Steam Generator		1,070	-
		Reactor Total		5,420	-
		Reactor System (10)		54,200	-
		Propane (Heating)		-	2,720 [2]
		Subtotal		77,900	174,350 [3]
		Contingency (15%)		11,700	198,700
		TOTAL		89,600	198,700

1 Since 32 days per lagoon are required it was assumed that 9 lagoons per year are processed rather than 11

2 Assume 5% of Capital Cost for Operating and Maintenance

3 Excludes rental of tanks and delivery charges which vary with location (Campbell, 1983)

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TABLE 19. COST ESTIMATES - LIQUID/LAGOON ANAEROBIC BIOLOGICAL TREATMENT (CASE ONE)

ALTERNATIVE	OPERATION	ITEM	BASIS	CAPITAL COST ($/lagoon)	OPERATING COST ($/lagoon)
Basic	Initial Materials	Dredging	17 days	11,000	7,400
	Secondary Materials	Suspension System (Intermittent)	120 days	8,650	13,950
	Conversion	Sludge Feed System	31 gph	360	75
		Subtotal		20,010	21,450
		Contingency (15%)		3,000	-
		TOTAL		23,000	21,450
Sidestream (Thermophillic)	Initial Materials	Dredging	17 days	11,000	7,400
	Secondary Materials	Suspension System	128 days	8,650	13,950
	Conversion	Reactor:	128 days		
		Closed Reactor		13,150	-
		Preheater		440	-
		Heat Exchanger		280	-
		Sludge Feed System		530	-
		Steam Generator		2,320	-
		Reactor Total		16,720	-
		Reactor System (10)		167,200	- 2
		Propane (Heating)		-	8,400
		Subtotal		186,900	174,350
		Contingency (15%)		28,000	204,100
		TOTAL		214,900	204,100

1 Since 128 days per lagoon are required it was assumed that 2-1/2 lagoons per year are processed rather than 11

2 Assume 5% of Capital Costs for Operating and Maintenance

3 Excludes rental and delivery cost of tanks which vary with location (Campbell, 1983)

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TABLE 19. CHEMICAL COSTS BY CONVERSION PROCESS

CHEMICAL	CONVERSION PROCESS	CONCENTRATION AVAILABLE (in solution)	UNIT COST	TOTAL REQUIREMENT	TOTAL COST ($/lagoon)
Sodium Sulfide ($Na_2S \cdot 9H_2O$)	Chemical Reduction	100%*	$ 240/Ton	218 Tons	52,320
Formic Acid	Chemical Reduction	90%	$ 0.90/lb	185,840 lbs	167,256
Hydrazine-Hydrate	Chemical Reduction	85%	$ 1.60/lb	53,470	85,550
Hydrogen Peroxide	Chemical Reduction	50%	$ 0.2635/lb	39,900 lb	22,630
Sodium Hydroxide	Complexing	50%	$ 240/Ton	4,000 lbs	60,210
	Alkaline Digestion	50%	$ 240/Ton	63.7 Tons	15,290
Surfactant Duoquad T-50	Complexing	100%	$ 1.16/lb	51,905 lbs	60,210
Sulfuric Acid	Complexing	98%	$ 60/Ton	0.625 Ton	38
	Alkaline Digestion	98%	$ 60/Ton	39 T (NaOH)	2,340
	Alkaline Digestion	98%	$ 60/Ton	94 T (NaOH)	5,660
Ammonium Hydroxide	Alkaline Digestion	30%	$ 210/Ton	224 Tons	47,100

*Available as a solid.

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TABLE 20. COST SUMMARY

ALTERNATIVE	CONTACTING METHOD (Table No.)	CAPITAL COST ($/lagoon)	OPERATING COST ($/lagoon)	TOTAL COST ($/lagoon)
Chemical Reduction	Solid Phase (7)	1,063,500	422,250	1,485,800
	Liquid/Lagoon (8)	28,240	93,950	122,200
	Liquid/Sidestream (9)	32,050	107,400	139,500
Complexing-Hydrolysis	Liquid/Lagoon (10)	28,240	69,100	97,400
	Liquid/Sidestream (11)	32,050	82,530	114,600
Alkaline Digestion	Liquid/Lagoon (12)	17,070	20,030	37,100
	Liquid/Sidestream (13)	20,600	21,500	42,100
Gamma Irradiation	Liquid/Sidestream (14)	24,800	31,300	56,100
Incineration	Liquid/Sidestream (15)	25,600	64,130	89,700
Wet-Air Oxidation	Liquid/sidestream (16)	127,400	104,350	231,800
Aerobic Biological	Liquid/Lagoon (17)	28,240	21,650	49,900
	Liquid/Sidestream (17)	89,600	198,700	288,300
Anaerobic Biological	Liquid/Lagoon (18)	23,000	21,450	44,500
	Liquid/Sidestream (18)	214,900	204,100	419,000

biological treatment alternatives. The reason for these differentials is the cost of fuel (propane) for heat addition and the number of reactors (10) required for sidestream treatment; the number of reactors is dependent upon reaction rates that were estimated conservatively (Volume Two) in the absence of definitive information.

The major element in the $130,000-per-lagoon cost of the wet air oxidation system is the unit itself. In comparison, the capital costs for the various chemical-based conversion or complexing systems are in the range of $25,000 to $32,000 per lagoon.

The capital costs for materials handling vary in magnitude from $14,000 to $24,000 for the liquid/lagoon and liquid/sidestream methods. These costs, viewed as nominal in magnitude, are very dependent on the costs of safety procedures that will be required after field studies are conducted.

Operating Costs

Operating costs are presented in Tables 7 to 18 and summarized in Table 20. From review of these, it is evident that the greatest cost ($422,000 per lagoon) is associated with the solid phase chemical reduction method of desensitization. As a general trend, the least operating costs are associated with the lagoon biological methods and with alkaline digestion ($21,000 per lagoon); these costs increase to $60,000 to $80,000 per lagoon for incineration and complexing hydrolysis methods and to $100,000 or more for wet-air oxidation and chemical reduction. Operating costs for the sidestream biological alternatives are on the order of $200,000 per lagoon due to the cost of heat needed to maintain the temperature in the thermophilic range.

Total Costs

The total per-lagoon cost estimates presented in Table 20 vary from $1.5 million for solid phase chemical reduction, $288,000 to $419,000 for the sidestream biological conversion processes, $230,000 for wet-air oxi-

dation and $120,000 to $140,000 for liquid phase chemical reduction to as little as $40,000 to $56,000 for liquid-lagoon biological treatment, alkaline digestion and gamma irradiation. It is apparent from these comparisons that the latter approaches (biological treatment, alkaline digestion and gamma irradiation) are most attractive from the cost basis used in this report.

DISCUSSION

The preceding analysis represents a first-pass assessment of the relative costs of desensitization. It is evident from the analysis that there is significant differentiation among the alternatives even at this level of analysis. It is also evident that developmental studies are required before a substantive preliminary engineering analysis can be made for each of the alternatives. It is probable that such studies will modify the relative ranking of the various alternatives but not change significantly the overall outcome. Nonetheless, the dollar cost estimates developed at each step should be used to establish priorities for the next level of development.

The results of the preceding cost analysis are weighty evidence that the greatest cost impact from developmental research will be in the following areas:

o   Conduct of bench-scale studies to define the kinetic (rate) characteristics, as applicable, for the biological and chemical conversions of TNT, RDX, HMX and nitrocellulose.

o   Design of field-scale tests to confirm the efficacy of the proposed water control and contacting methods for liquid/lagoon (i.e., insitu) desensitization.

o   Developmental studies to conceptualize and design on a preliminary basis the safety procedures attendant to insitu desensitization

Additional discussion leading to specific recommendations is presented after the evaluations of Chapter 6.

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CHAPTER 6

EVALUATION OF ALTERNATIVES

The desensitization alternatives are evaluated and rated in this chapter by comparison for favorable, moderate, or unfavorable impact relative to each of the performance measures defined in Chapter 2. In the majority of the alternatives the standard (Case One) lagoon scenario was used for the design basis, except where the inflexibility of a process necessitated the utilization of another case. The applicable alternatives are rank-ordered; the efficacy of the alternative for each of the other lagoon scenarios is then assessed, and the alternatives rank-ordered on the basis of indicated feasibility.

PERFORMANCE MEASURES

Each proposed performance measure was defined in Chapter 2 and is defined further below.

Cost

Estimated capital and operating costs for each alternative were tabulated and evaluated by comparison. The following ranges were used for the ranking:

Ranking	Total Cost
Favorable	$ 37,000 - $ 60,000
Moderate	$ 61,000 - $ 199,000
Unfavorable	$200,000 - $1,500,000

Flexibility

Flexibility is used to indicate how many of the explosives of concern can be desensitized by the alternative. The following ranking was applied:

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Ranking	Applicable Explosives
Favorable	All
Moderate	Most, more than two
Unfavorable	One to two

State-of-the-Art

This is a measure of the development status of the alternative. The technology exists for all the alternatives although in most cases it must be adopted and modified from another application. The term "technology" in this sense refers broadly to equipment or methods including those based upon chemical dosages or chemical/biological rates. The following criteria was used to evaluate state-of-the-art.

Ranking	Criteria
Favorable	Technology is proven in similar applications, on-line or in pilot studies. The least amount of developmental work is required.
Moderate	Technology is proven in other applications; a large amount of laboratory studies and some pilot studies have been performed. Some development work required (laboratory, pilot and field).
Unfavorable	Technology is on a theoretical basis or demonstrated by few laboratory scale studies. A large amount of laboratory, pilot and field scale development is required.

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Degree of Desensitization

This performance measure is difficult to evaluate inasmuch as a working definition of "desensitization" remains to be developed. It was, therefore, conservatively assumed that alternatives which totally transform or cleave the molecular structure of the explosive accomplish a high degree of desensitization. Those which desensitize by converting or substituting the nitro groups achieve a lower degree of desensitization, inasmuch the extent of the conversion or substitution (number of nitro groups affected) is difficult to measure.

The following rankings were used:

Ranking	Criteria
Favorable	Explosive molecule is cleaved or totally transformed
Moderate	One or all nitro groups on explosive molecule are converted or substituted.
Unfavorable	Same basis as the moderate ranking except that the degree of contacting provided by the alternative will most likely be insufficient for all molecules to react Overall, many explosive molecules will remain unaffected.

Implementation Time

This is a measure of the overall time requirement for the implementation of the alternative. Implementation time is equal to the sum of mobilization (transportation, assembly, start-up), processing, and demobilization (shut-down, disassembly) times. The following criteria were used to evaluate implementation time.

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Ranking	Criteria
Unfavorable	Technology which requires special handling (transportation and assembly) procedures and a large amount of site preparation. Also includes desensitization done at a relatively slow rate.
Moderate	Alternatives in which desensitization occurs in a continuous sidestream at moderate processing rates.
Favorable	Alternatives performed in a lagoon or sidestream at relatively fast processing rates.

Complexity

Complexity is a subjective measure relating to operating and maintenance requirements. The following criteria were used to evaluate complexity.

Ranking	Criteria
Unfavorable	Technology which has a history of high maintenance requirements, excessive downtime and requires a skilled operator present at all times.
Moderate	Technology which has a relatively large amount of equipment (sidestream processing) or a small amount of equipment but a history of maintenance problems.

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Favorable	Technology requires a minimum amount of equipment (insitu lagoon) and operator skill and attention.

Risk Acceptability

This is an aggregate measure of safety hazards to personnel involved in all the stages of implementation of the alternative. Safety hazards include explosive potential, radiation, flammability, toxic fumes and toxic reactants, products and byproducts. The following assumptions were made:

o   The hazard of processing undiluted sediment is greater than the hazard of processing diluted sediment.

o   The use of radiation presents a potential personnel hazard

o   The total hazard is increased by an increasing amount of equipment and complexity of operation.

o   Alternatives which use toxic chemicals and generate toxic products or byproducts increase the hazard potential.

Alternatives were evaluated by cumulating the number of hazard opportunities in each processing step. Rankings were based upon the following criteria:

Ranking	Criteria
Favorable	None of the assumed hazardous conditions apply.
Moderate	One of the assumed hazardous conditions apply.
Unfavorable	More than one of the assumed hazardous conditions apply.

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Disposability

Disposability is a measure of the environmental risk and impact of the materials and processes used for desensitization combined with the risk and impact of the products and byproducts of desensitization. The form, toxicity and mobility of the compounds are taken into consideration.

The following factors characterizing the form, mobility and toxicity were used to evaluate this performance measure:

o   Possible contamination of surface or underground aquifers
       (mobility).

o   Toxic air emissions (unless an enclosed reactor is used).

o   Toxicity of chemicals used to desensitize

o   Toxicity of products of desensitization

o   Toxicity of byproducts of desensitization

o   The requirement for post-desensitization treatment

The following criteria were used for ranking purposes:

Ranking	Criteria
Favorable	None or one of the above factors apply.
Moderate	Two or three of the above factors only.
Unfavorable	More than three of the above factors apply.

EVALUATIONS

Evaluations for each desensitization alternative are presented in Table 21; comments on each evaluation are presented below:

TABLE 21. RANKING OF DESENSITIZATION ALTERNATIVES BY PERFORMANCE MEASURE RATINGS

ALTERNATIVE	COST	FLEXIBLE	STATE OF ART	DEGREE OF DESEN'N	IMPLEMENTATION	COMPLEXITY	RISK ACCEPTABILITY	DISPOSABILITY
Chemical Reduction								
Solid Phase	U	F	U	U	U	M	F - M	M - U
Liquid/Lagoon	M	F	U	M	F	F	F - M	M - U
Liquid/Sidestream	M	F	U	M	M	M	M - U	M - U
Complexing-Hydrolysis								
Liquid/Lagoon	M	M	M	M	F	F	M	M
Liquid/Sidestream	M	M	M	M	M	M	U	M
Alkaline Digestion								
Liquid/Lagoon	F	U	M	P	F	F	M	M
Liquid/Sidestream	F	U	M	P	F	M	M	M
Gamma Irradiation	F	F	M	F	M	M	U	F
Aerobic Biological								
Liquid/Lagoon	P	U	U	M	M	F	F	M
Liquid/Sidestream	U	U	U	M	M	M	M	M
Thermophillic								
Anaerobic Biological								
Liquid/Lagoon	P	M	U	M	U	P	M	M
Liquid/Sidestream	U	M	U	M	U	M	M	M
Thermophillic								
Incineration	M	F	M	P	M	M	M	M
Wet-Air Oxidation	U	F	F	P	U	U	M	F

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Chemical Reduction

The chemical reduction alternatives were found to be highly flexible; however, a lack of available information on chemical requirements (i.e., limited and contradictory literature information) indicates that a high degree of development is required (i.e., the state-of-the-art is "unfavorable"). The degree of desensitization achieved is "moderate" for the liquid phase alternatives and "unfavorable" for the solid phase due to limitations on efficiencies with bulk contacting. As in most alternatives, the implementation time is "favorable" for the insitu desensitization and "moderate" for the continuous sidestream reactor. Extensive site preparation effort for solid phase chemical reduction (an estimated one-month period is requ_red) warranted an "unfavorable" rating for implementation.

The risk acceptability and disposability measures are both dependent upon the reductant used; the use of the sodium sulfide reductant should result in toxic (hydrogen sulfide) emissions. The toxicity of the final products and byproducts are also dependent upon the choice of reductant. For these reasons two ratings ("unfavorable" and "moderate") were deemed to be warranted (Table 21).

Complexing-Hydrolysis

Complexing-hydrolysis alternatives are applicable to all explosives except nitrocellulose. This technology has been demonstrated on a pilot scale, although not for lagoon sediments. The desensitized TNT-surfactant complex is more toxic than either the TNT or surfactant itself; therefore, the risk acceptability and disposability ratings were "moderate." The combination of this toxicity and the additional equipment requirements for continuous sidestream desensitization (with attendant additional hazard) was the basis for a "unfavorable" risk rating for this alternative.

Alkaline Digestion

The cost of desensitization by alkaline digestion is rated as "favorable" due to the relatively low cost of the chemicals and the

requirement for minimal dilution of resuspended lagoon sediment. The implementation time and complexity of this alternative are rated as "favorable" and "moderate," respectively, for both the liquid/lagoon and sidestream alternatives. This is due to a relatively fast reaction rate and a minimum of equipment required for processing. The toxicity of products and byproducts is dependent upon the chemical used for the digestion and reaction parameters; the formation of nitrous oxides and cyanide is possible. The flexibility of these alternatives is "unfavorable", that is, limited to nitrocellulose.

Gamma Irradiation

Gamma irradiation is ranked as being a "favorable" cost and flexibility alternative for desensitization. This technology has been proven for sludge disinfection in an on-line demonstration project and for the desensitization of explosives in a laboratory study. Although a large amount of site preparation and operator attention is anticipated, this alternative is rated as "moderate" for both measures due to its high processing rate and performance history. Also, the site can be prepared prior to delivery of the unit. The combination of its capability for the processing of resuspended sediments after minimal dilution and the presence of radiation are reflected in a "unfavorable" risk rating. However, desensitized material from gamma irradiation is anticipated to be highly amenable to disposal.

Biological Treatment

Aerobic treatment is deemed to be inflexible because it is limited to TNT whereas anaerobic treatment is moderately flexible, being applicable for TNT, RDX and HMX but not for nitrocellulose. The cost of both types of treatment is "favorable" for the insitu alternatives, but "unfavorable" for the sidestream thermophilic alternatives. Both of these biological treatment methods have yet to be proven for sediment slurry desensitization; however, laboratory data are available for the anaerobic decomposition of explosive wastewaters and pilot/operating data for the aerobic treatment of TNT. Implementation time is "moderate" for aerobic treatment (30-32 days) but "unfavorable" for anaerobic treatment (120-128 days) because of the rate constants assumed. Risk acceptability is greater

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for anaerobic treatment because toxic off-gases may be generated, particularly if sodium sulfide addition is required to precipitate excess heavy metals and the sidestream alternatives requiring more equipment are deployed.

Incineration and Wet-Air Oxidation

Both of these alternatives are highly flexible, being applicable for all explosives. Incineration has been proven for similar applications but pilot testing on explosive-contaminated lagoon sediments remains to be performed. Wet-air oxidation pilot studies have been conducted successfully on propellent mixtures; both alternatives have a history of high maintenance requirements. However, as the explosive molecule is totally transformed, both alternatives were rated as achieving a "favorable" degree of desensitization. Implementation time was ranked as "moderate" for incineration (26 days to process the contents of the standard lagoon used in the scenario, Appendix D) and "unfavorable" for wet-air oxidation (a 50-day processing time with significant site preparation work, Appendix D).

RANK-ORDERING

To further examine the desensitization technologies, the applicable alternatives have been rank-ordered for each lagoon case example. The rank-ordering was based upon a rating assigned for each and all of the performance measures. All performance measures were treated equally with no weighting factors applied, although this possibility is open for future consideration. It should also be noted that the use of weighting factors (i.e., cost, flexibility, etc.) would impact significantly on the ranking.

The process of rank-ordering was expedited by using a numerical system to compile individual ratings. A numbering scale from 1 to 5 was used wherein a "1" was assigned to the more preferable rating (e.g., favorable). Scores were compiled in this manner for all measures and then added for each alternative. These totals were then compared and rank-ordered from

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compared and rank-ordered from the lowest to the highest total. This procedure was repeated for each case example; appropriate deletions or additions were made for each alternative depending upon the impact of the example scenario upon the alternative.

The rank-ordering of alternatives was done to provide a general comparison of the desensitization concepts and in many cases only a fine distinction can be made. Rank-ordering can only be as definitive as the design and cost basis of each alternative. Although the many assumptions required for this evaluation may qualify the outcome, the results nonetheless, provide a valuable basis for prioritizing further developmental work.

Case One

The rank-ordering of the alternatives for Case One was based upon the ratings shown in Table 21 and is presented in Table 22. Gamma irradiation and in-lagoon chemical reduction are the higher-ranked alternatives while in-lagoon complexing-hydrolysis and incineration are both rated equally. Wet-air oxidation is ranked higher than the in-lagoon anaerobic biological method. The remainder are all liquid/sidestream alternatives involving chemical reduction and complexing-hydrolysis. The lowest ranked alternatives are solid phase chemical reduction and liquid/sidestream anaerobic biological treatment.

Alkaline digestion and the aerobic biological treatment alternatives are not applicable to the Case one scenario.

Case Two

The only variation in Case Two from Case One is that the concentrations of explosives are reduced by 90 percent. The predominant impact of this change is a reduction in chemical requirements where applicable. The individual impact on each alternative is presented in Table 23.

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TABLE 22. RANKING OF ALTERNATIVES (CASE ONE)

RANK	ALTERNATIVE	CONTACTING METHOD
1	Gamma Irradiation	Liquid/Sidestream
1	Chemical Reduction	Liquid/Lagoon
2	Complexing-Hydrolysis	Liquid/Lagoon
2	Incineration	Liquid/Sidestream
3	Wet-Air Oxidation	Liquid/Sidestream
4	Anaerobic Biological	Liquid/Lagoon
4	Chemical Reduction	Liquid/Sidestream
5	Complexing-Hydrolysis	Liquid/sidestream
6	Chemical Reduction	Solid Phase
7	Anaerobic Biological	Liquid/Sidestream
N/A	Alkaline Digestion	All
N/A	Aerobic Biological	All

TABLE 23. IMPACT OF CASE TWO ON ALTERNATIVES

ALTERNATIVE	CONTACTING METHOD	MAJOR IMPACT
Chemical Reduction	All	Chemical requirements and costs reduced by 90%
Complexing-Hydrolysis	All	Surfactant requirement and cost reduced by 90%
Alkaline Digestion	All	N/A
Gamma Irradiation	Liquid/Sidestream	Shorter Retention Time
Incineration	Liquid/Sidestream	Slight increase in supplemental fuel requirement
Wet-Air Oxidation	Liquid/Sidestream	None
Anaerobic Biological	All	Shorter retention time

The ratings shown in Table 21 were also used to rank-order the alternatives for Case Two (and all subsequent cases). Modifications in the individual ratings were made based upon the impact of the Case Two scenario on the alternative. The reduced cost of chemicals was taken into account by lowering the cost ratings for chemical reduction (lagoon and sidestream) and for complexing-hydrolysis. The cost of solid-phase chemical reduction was not sufficiently impacted to warrant changing; the same is true of the other listed impacts with respect to gamma irradiation, incineration and wet air oxidation.

The revised rank-order is shown in Table 24. The liquid/lagoon chemical reduction alternative is indicated as highest-ranked, and complexing-hydrolysis is ranked equally with gamma irradiation.

Case Three

In Case Three the lagoon liner is removed and a high water table assumed. This variation is assumed to eliminate all of the insitu lagoon alternatives due to the likelihood of groundwater contamination.

The major impacts on the individual alternatives are reported in Table 25. All the insitu lagoon and solid phase alternatives are eliminated and holding tanks are required for the remaining alternatives. It is assumed that sediment will be excavated and stored at a minimum level of dilution for all the alternatives. If required the sediment will be diluted as it is transferred to the sidestream reactor. For this reason the cost of a holding tank is the same for all alternatives and no modifications are required relative to Case One.

The revised rank-order is shown in Table 26. As expected the ranking is unaffected except for the elimination of the alternatives assumed to be infeasible.

Case Four

The only variation in Case Four is that the soil/sediment is assumed to have a high clay content with the assumed impacts that it is less permeable

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TABLE 24. RANKING OF ALTERNATIVES (CASE TWO)

RANK	ALTERNATIVE	CONTACTING METHOD
1	Chemical Reduction	Liquid/Lagoon
2	Gamma Irradiation	Liquid/Sidestream
2	Complexing-Hydrolysis	Liquid/Lagoon
3	Incineration	Liquid/Sidestream
4	Chemical Reduction	Liquid/Sidestream
4	Wet Air Oxidation	Liquid/Sidestream
5	Anaerobic Biological	Liquid/Lagoon
5	Complexing-Hydrolysis	Liquid/Sidestream
6	Chemical Reduction	Solid/Phase
6	Anaerobic Biological	Liquid/Sidestream

TABLE 25. IMPACT OF CASE THREE ON ALTERNATIVES

ALTERNATIVE	CONTACTING METHOD	MAJOR IMPACT
Chemical Reduction	Solid Phase	Infeasible
	Liquid/Lagoon	Infeasible
	Liquid/Sidestream	Holding basin required
Complexing Hydrolysis	Liquid/Lagoon	Infeasible
	Liquid/Sidestream	Holding basin required
Alkaline Digestion	All	N/A
Gamma Irradiation	Liquid/Sidestream	Holding basin required
Incineration	Liquid/Sidestream	Holding basin required
Wet-Air Oxidation	Liquid/Sidestream	Holding basin required
Aerobic Biological	Liquid/Lagoon	N/A
Anaerobic	Liquid/Lagoon	Infeasible
	Liquid/Sidestream	Holding basin required

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TABLE 26. RANKING OF ALTERNATIVES (CASE THREE)

RANK	ALTERNATIVE	CONTACTING METHOD
1	Gamma Irradiation	Liquid/Sidestream
2	Incineration	Liquid/Sidestream
3	Wet-Air Oxidation	Liquid/Sidestream
4	Chemical Reduction	Liquid/Sidestream
5	Complexing-Hydrolysis	Liquid/Sidestream
6	Anaerobic Biological	Liquid/Sidestream

and requires a greater amount of dilution to be pumpable. The individual impacts for each alternative are shown in Table 27. Solid phase chemical reduction is assumed to be infeasible for this scenario. Larger volumes of materials will have to be processed even in alternatives such as gamma irradiation and incineration that can handle the higher sediment solids concentrations. In the case of incineration, the cost ranking of Table 21 was increased to reflect the additional cost of supplemental fuel or of providing a dewatering process. The cost of gamma irradiation is unaffected because the processing rate can be increased and the required dosage of gamma radiation will not be significantly affected by dilution of the sediment.

The revised rank-ordering for the Case Four scenario is presented in Table 28. The only change is that the expected added cost of incineration results in its achieving an equal ranking to wet-air oxidation.

Case Five

Case Five differs from Case One by the presence of toxic heavy metals and lagoon conditions which require high dilution of the sediments. It was assumed that for dredging to be feasible, a dilution of sediments to 5 to 10% solids is required.

The individual impact on each alternative is presented in Table 29. Only a minimal impact is anticipated on the chemical reduction and anaerobic biological alternatives; the major impact will be upon incineration. Hydraulic classification and dewatering of the lagoon slurry will be required prior to incineration. The liquid fraction from this separation will contain solubilized explosives requiring end-of-pipe treatment. For these reasons the cost and risk acceptability ratings in Table 21 were increased for the incineration alternative. Complexity and disposability were not increased because these measures were already set at the maximum ratings.

The overall processing time required for gamma irradiation may increase; however, a large increase is also anticipated in the processing

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TABLE 27. IMPACT OF CASE FOUR ON ALTERNATIVES

ALTERNATIVE	CONTACTING METHOD	MAJOR IMPACT
Chemical Reduction	Solid Phase	Infeasible
	Liquid/Lagoon	None
	Liquid/Sidestream	None
Complexing-Hydrolysis	All	None
Alkaline Digestion	All	NA
Gamma Irradiation	Liquid/Sidestream	Larger volume to process
Incineration	Liquid/Sidestream	Additional supplemental fuel or dewatering is required
Wet-Air Oxidation	Liquid/Sidestream	None
Aerobic Biological	All	N/A
Anaerobic Biological	All	None

TABLE 28. RANKING OF ALTERNATIVES (CASE FOUR)

RANK	ALTERNATIVE	CONTACTING METHOD
1	Gamma Irradiation	Liquid/Sidestream
1	Chemical Reduction	Liquid/Lagoon
2	Complexing-Hydrolysis	Liquid/Lagoon
3	Incineration	Liquid/Sidestream
3	Wet-Air Oxidation	Liquid/Sidestream
4	Anaerobic Biological	Liquid/Lagoon
4	Chemical Reduction	Liquid/Sidestream
5	Complexing-Hydrolysis	Liquid/Sidestream
6	Anaerobic Biological	Liquid/Sidestream

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TABLE 29. IMPACT OF CASE FIVE ON ALTERNATIVES

ALTERNATIVE	CONTACTING METHOD	MAJOR IMPACT
Chemical Reduction	All	Minimal; increased chemical demand to complex toxic metals
Complexing Hydrolysis	All	None
Alkaline Digestion	All	N/A
Gamma Irradiation	Liquid/Sidestream	Very large volume to process; process rate increases
Incineration	Liquid/Sidestream	Large supplement fuel cost or else need to install dewatering/classification
Wet-Air Oxidation	Liquid/Sidestream	None
Aerobic Biological	All	N/A
Anaerobic Biological	All	Minimal; chemical needed to complex toxic metals

rate. It is therefore assumed that the increase in implementation time does not warrant a rating modification.

The revised rank order is shown in Table 30 with incineration now ranked below wet-air oxidation because of the greater dilution of sediment assumedly required.

Case Six

Case Six consists of a lagoon that is 10-fold larger in volume than the Case One scenario but has explosives concentrations 10-fold lower since the total weight of explosives is equivalent in each scenario. The impacts of the Case Six assumptions are presented in Table 31; the major impact for all alternatives is an increased initial materials handling cost.

The major impact of the Case Six assumptions is on the sidestream alternatives. Although the chemical requirements are unchanged for these alternatives, a similar amount of retention time is necessary to ensure contacting. Accordingly, the ratings of the chemical reduction and complexing-hydrolysis alternatives for implementation time were increased. The increased volume results in increases in supplemental fuel cost and implementation time for incineration; therefore, the ratings of both of these measures were increased. Gamma irradiation was unaffected since the penetrating power of gamma radiation is unaffected by the presence of additional solids.

The revised rank-ordering of alternatives for the Case Six scenario is presented in Table 32. Incineration is again ranked lower than wet-air oxidation.

Case Seven

In this scenario the only explosive assumed to be present in the sediment is nitrocellulose. The major overall impact is that the total weight of explosives to be desensitized is reduced; thus, most of the chemical requirements are reduced.

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TABLE 30. RANKING OF ALTERNATIVES (CASE FIVE)

RANK	ALTERNATIVE	CONTACTING METHOD
1	Gamma Irradiation	Liquid/Sidestream
1	Chemical Reduction	Liquid/Lagoon
2	Complexing-Hydrolysis	Liquid/Lagoon
3	Wet-Air Oxidation	Liquid/Sidestream
4	Incineration	Liquid/Sidestream
4	Anaerobic Biological	Liquid/Lagoon
4	Chemical Reduction	Liquid/Sidestream
5	Complexing-Hydrolysis	Liquid/Sidestream
6	Chemical Reduction	Solid Phase
7	Anaerobic Biological	Liquid/Sidestream

TABLE 31. IMPACT OF CASE SIX ON ALTERNATIVES

ALTERNATIVE	CONTACTING METHOD	MAJOR IMPACT
Chemical Reduction	Solid Phase	Cost increase for more wells
	Liquid/Lagoon	None
	Liquid/Sidestream	Processing time increases
Alkaline Digestion	All	N/A
Complexing-Pyrolysis	Liquid/Sidestream	Processing time increases
Gamma Irradiation	Liquid/Sidestream	Processing rate increases
Incineration	Liquid/Sidestream	Supplemental fuel increases
Wet-Air Oxidation	Liquid/Sidestream	Processing time increases
Aerobic Biological	All	N/A
Anaerobic Biological	All	None

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TABLE 32. RANKING OF ALTERNATIVES (CASE SIX)

RANK	ALTERNATIVE	CONTACTING METHOD
1	Gamma Irradiation	Liquid/Sidestream
1	Chemical Reduction	Liquid/Lagoon
2	Complexing-Hydrolysis	Liquid/Lagoon
3	Wet-Air Oxidation	Liquid/Sidestream
4	Incineration	Liquid/Sidestream
4	Anaerobic Biological	Liquid/Lagoon
5	Chemical Reduction	Liquid/Sidestream
6	Complexing-Hydrolysis	Liquid/Sidestream
7	Chemical Reduction	Solid Phase
8	Anaerobic Biological	Liquid/Sidestream

The individual impacts for each alternative are shown in Table 33. All biological alternatives are infeasible for this scenario because nitrocellulose requires chemical treatment as an initial decomposition step. In addition all complexing-hydrolysis alternatives are also infeasible. The cost of all chemical reduction alternatives is decreased; therefore, the cost ratings of Table 21 for the lagoon and sidestream contacting methods were decreased. The cost of solid phase chemical reduction was not sufficiently reduced to warrant a rating modification. No other impacts were deemed to be signficant.

The revised rank-order is shown in Table 34. Chemical reduction is highest-ranked. Gamma irradiation and alkaline digestion (in the lagoon) are next-ranked followed by sidestream alkaline digestion and incineration. Sidestream chemical reduction and wet-air oxidation are the lowest ranked alternatives.

Case Eight

This scenario is identical to Case One but with the deletion of RDX from the lagoon. The total weight of explosives in the sediment is therefore reduced and the individual impact on each alternative is presented in Table 35. Aerobic biological treatment is feasible because only TNT is present. The cost of chemical reduction alternatives is partially lowered but not enough to affect the cost rating. Likewise, none of the other impacts affect the ratings of Table 21.

The revised rank order for the Case Eight example is presented in Table 36. The only modification to the Case One rank-order is that aerobic biological treatment in the lagoon and in a sidestream are included and are ranked as third and seventh respectively.

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TABLE 33. IMPACT OF CASE SEVEN ON ALTERNATIVES

ALTERNATIVE	CONTACTING METHOD	MAJOR IMPACT
Chemical Reduction	All	Lower chemical requirements and cost
Complexing-Hydrolysis	All	**Infeasible**
Alkaline Digestion	All	Feasible
Gamma Irradiation	Liquid/Sidestream	Increase processing rate
Incineration	Liquid/Sidestream	Slight increase in supplement fuel requirement
Wet-Air Oxidation	Liquid/Sidestream	None
Aerobic Biological	All	Infeasible
Anaerobic Biological	All	Infeasible

TABLE 34. RANKING OF ALTERNATIVES (CASE SEVEN)

RANK	ALTERNATIVE	CONTACTING METHOD
1	Chemical Reduction	Liquid/Lagoon
2	Gamma Irradiation	Liquid/Sidestream
2	Alkaline Digestion	Liquid/Lagoon
3	Alkaline Digestion	Liquid/Sidestream
3	Incineration	Liquid/Sidestream
4	Chemical Reduction	Liquid/Sidestream
4	Wet-Air Oxidation	Liquid/Sidestream

TABLE 35. IMPACT OF CASE EIGHT ON ALTERNATIVES

ALTERNATIVE	CONTACTING METHOD	MAJOR IMPACT
Chemical Reduction	All	Lower chemical requirements and cost (slightly)
Complexing-Hydrolysis	All	None
Alkaline Digestion	All	N/A
Gamma Irradiation	Liquid/Sidestream	Slight increase in processing rate
Incineration	Liquid/Sidestream	Slight increase in amount of supplemental fuel
Wet-Air Oxidation	Liquid/Sidestream	None
Aerobic Biological	All	Feasible
Anaerobic Biological	All	None

TABLE 36. RANKING OF ALTERNATIVES (CASE EIGHT)

RANK	ALTERNATIVE	CONTACTING METHOD
1	Gamma Irradiation	Liquid/Sidestream
1	Chemical Reduction	Liquid/Lagoon
2	Complexing Hydrolysis	Liquid/Lagoon
2	Incineration	Liquid/Lagoon
3	Aerobic Biological	Liquid/Lagoon
3	Wet-Air Oxidation	Liquid/Sidestream
4	Anaerobic Biological	Liquid/Lagoon
4	Chemical Reduction	Liquid/Sidestream
5	Complexing Hydrolysis	Liquid/Sidestream
6	Chemical Reduction	Solid Phase
7	Aerobic Biological	Liquid/Sidestream
7	Anaerobic Biological	Liquid/Sidestream

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

This investigation was structured as an identification of
desensitization technologies, development of alternatives incorporating
these technologies and evaluation of the alternatives using selected
performance measures and incineration as a baseline technology. The
conclusions and recommendations presented in this chapter were influenced
in large part by the application of the selected measures.

CONCLUSIONS

The following conclusions were drawn from the evaluations presented in
this report:

(1) Gamma irradiation and the insitu chemical conversion alternatives
    for reduction, complexing-hydrolysis and alkaline digestion were
    consistently ranked higher than incineration, the baseline
    desensitization alternative.

(2) Gamma irradiation is an attractive desensitization alternative
    beause it was found to be low in cost and very flexible, i.e.,
    minimally impacted in performance capability over wide ranges of
    concentration of explosive and of the sediment matrix for the
    explosives.

(3) Chemical reduction is a preferred method because it can be used in
    conjunction with all the contacting methods and for all the
    explosives evaluated in this investigation.

(4) Chemical treatment (by means of reduction or complexing-
    hydrolysis) is a promising method for sediments containing

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relatively low (one to 10 percent) concentrations of explosives, because the performance of these processes is more dependent upon the weight of explosives being desensitized than on the volume of materials being processed.

(5) Incineration and wet-air oxidation are indicated to be more cost-effective in the treatment of sediments with relatively high explosive contents (greater than 10 percent); their cost-efficiency diminishes with decreasing explosive content.

(6) Alkaline digestion may not be feasible in the presence of TNT; therefore, the development of this process as a desensitization technique for sediments containing nitrocellulose is warranted only if enough lagoons containing this explosive but not TNT are identified.

(7) Although biological alternatives for desensitization were evaluated using all available data, these alternatives cannot be compared reasonably with chemical and thermal methods until treatability studies for determination of rate constants are conducted.

(8) Solid phase desensitization is costly relative to liquid phase methods but is applicable in cases where soil/sediments cannot be disturbed.

(9) When a desensitization method is feasible using liquid phase contacting in either the lagoon or as a sidestream, the lagoon (insitu) method is preferred because the handling, equipment requirements, implementation time, and cost factors are generally lower for insitu processing.

(10) Of the undeveloped concepts, lagoon detonation and open burning result in uncontrolled air emissions; therefore, surfactant-oil complexing may be appropriate if the final material can be incinerated under controlled conditions.

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RECOMMENDATIONS

The evaluations presented in this report were developed using
information on technologies that in several cases was preliminary at best.
Nonetheless, it has become apparent as a result of these evaluations that:

(1) alternatives incorporating gamma irradiation and chemical
     reduction are most promising;

(2) alternatives incorporating biological transformation may become
     promising upon further elaboration of the kinetics, as opposed to
     the mechanism, of desensitization; and

(3) alternatives incorporating surfactant/oil complexing,
     iron-peroxide oxidizing solutions (Fenton's Reagent), and alkaline
     digestion may become promising upon further elaboration of
     specific mechanisms or constraints delimiting their current
     acceptance.

Accordingly, the following bench-scale studies are recommended for the
development of baseline data in descending order of priority.

Gamma Irradiation Treatment

A series of bench-scale experiments are recommended to determine the
dosage of gamma radiation required to desensitize explosives. The initial
experiments should determine the dosage requirements for desensitizing dry
samples of varying concentrations of TNT, RDX and nitrocellulose enabling a
basic relationship to be established. Subsequent experiments should
determine the impact of moisture content (10-50 percent) temperature (20 to
$60^{o}C$), and chemical solutions (Fenton's Reagent) on the basic dosage
requirement.

Chemical Reduction

Studies are recommended to identify specific chemical reductants,
cost-effective dosages and reaction conditions for explosive
desensitization. Initial experiments should continue the previous

developmental work performed under Army contract. In particular, the
dosage and detention requirements of hydrazine, sodium sulfide and formic
acid should be determined for dese tizing TNT, RDX and nitrocellulose.
The effect of temperature, pH and organic solvents (solubility enhancement)
on reductant dosages should also be determined.

Alkaline Digestion

Bench-scale studies are recommended to determine the effect of alkaline
digestion on TNT (the literature indicated that a more sensitive compound
may be formed by the reaction of alkali and TNT). If this concept is
limited to desensitization of TNT, a decision on the justification of
further development of alkaline digestion is needed.

Fenton's Reagent/Oil-Surfactant Complexing

Bench-scale experiments are recommended for the purpose of determining
the feasibility of each concept. Initial experiments should determine the
dosage and detention requirements of each concept for desensitization
of TNT, RDX and nitrocellulose. Subsequent experiments should investigate
the use of Fenton's Reagent in combination with gamma irradiation and
oil-surfactant complexing for desensitizing of high concentrations of
explosives.

Anaerobic and Aerobic Biological Treatment

Bench-scale studies are recommended for the purpose of conducting
biological treatability studies to determine the rate constants for
biotransformation of explosives to desensitized end products. The aerobic
biotransformation rates of TNT and the anaerobic biotransformation rate of
TNT, RDX and HMX should be defined over temperature ranges from 10 to 60°C,
under nutrient-sufficient conditions, and for solutions saturated and
unsaturated with respect to each of these explosives.

CHAPTER 8

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SUPPLEMENTARY

INFORMATION

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